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3,239,454 SELECTIVE MULTISTAGE HYDROGENATION OF HYDROCARBONS

Carl W. Streed, Haddonfield, and Raymond R. Halik,
Pitman, N.J., assignors to Socony Mobil Oil Company,
Inc., a corporation of New York
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The present invention relates to a process, preferably in 3 or more catalytic stages of a normally liquid hydrocarbon mixture containing aromatic hydrocarbons, olefins, diolefins, sulfur compounds and possibly acetylenes.

Many processes for the selective hydrogenation of petroleum hydrocarbons in a nondestructive manner, that is hydrogen addition with little or no cracking or hydrocracking of the feed, have been advanced over the years. Interest in this field has intensified in the last decade with the advent of catalytic hydroforming which has made large supplies of hydrogen-rich gas available at refineries at a relatively low cost which might be charged at least in part against the improvement of naphthas in the reforming operation.

Selective hydrogenation serves many purposes and the instant invention is particularly concerned with a preferred embodiment in which an unstable hydrocarbon mixture of the type mentioned above containing a high proportion of aromatic hydrocarbons is hydrogenated in at least two stages of increasing severity to prepare a stable product from which valuable aromatic hydrocarbons can readily be separated, for example, by solvent extraction with a solvent such as diethylene glycol. In such extractions it is relatively easy to separate benzene and other aromatic compounds from paraffinic hydrocarbons but this is not true of separating benzene from aliphatic and cycloaliphatic unsaturated components, and especially from organic sulfur compounds, in the mixture.

To prepare a suitable feed for the solvent extraction of aromatics, 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. Although it is simple to specify the reactions with hydrogen for obtaining these results, achieving them in commercial practice has been an entirely different matter. There is an increasing demand for the production of aromatic hydrocarbons from petroleum so that the supplies of these compounds are not restricted to the current production level of the steel and coking industries. Despite this demand, prior to the present invention there was still no fully satisfactory commercial method for the hydrogenation of such mixtures of aromatic and unsaturated aliphatic hydrocarbons.

It is not feasible to completely saturate and desulfurize such feed stocks in a single operation because the relatively high temperatures suitable for hydrodesulfurization also promote the formation of coke and olefin polymers (gums) and may hydrogenate aromatics to naphthenes under certain conditions. Prior to the present invention even conducting the hydrogenation reactions in several stages to avoid or minimize the aforesaid deficiencies has not been entirely satisfactory by reason of the accumulation of polymeric deposits that reduce the activity of hydrogenation catalysts, thereby requiring frequent regeneration, and in addition these 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 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.

An object of the present invention is to provide an improved process for the selective hydrogenation of mixed organic compounds.

Still another object of the invention is to provide an improved process for the selective, nondestructive hydrogenation of a mixture of aromatic and olefinic hydrocarbons boiling below about 500° F., and preferably below about 275°, in which contact catalysts are kept on stream for substantially longer periods.

A further object of the invention is to provide an improved process for the selective catalytic hydrogenation of a mixture of aromatic and olefinic hydrocarbons in two or more reactors in which the on-stream periods of all reactors are lengthened.

Other objects and advantages of the invention will be apparent to those skilled in the art upon consideration of the following detailed disclosure in which all temperatures are expressed in terms of degrees Fahrenheit, all proportions in terms of weight and all temperatures of boiling points or ranges are measured at atmospheric pressure by the A.S.T.M. procedure unless otherwise expressly stated hereinafter.

The present invention is an improved method for the selective, nondestructive hydrogenation of a hydrocarbon liquid boiling below about 500°, which contains aromatic hydrocarbons, preferably in relatively large amounts, and also olefins, diolefins and sulfur compounds. It comprises reacting said material substantially in the liquid phase with hydrogen in contact with a porous solid hydrogenation catalyst of high hydrogenation activity and low polymerization activity in an initial hydrogenation zone while controlling the hydrogenating conditions therein to provide an initial hydrogenation effluent in which a substantial amount that may be at least about 35% of the diolefins, and preferably at least about 50%, have been at least partially saturated and in which a substantial part of said liquid feed and products thereof remain in the liquid phase. This liquid phase may be at least about 20% and preferably at least about 60% of the liquid feed. In a preferred modification, the Bromine Number of the normally liquid fraction of said effluent is also reduced at least about 25% below that of the liquid feed. After vaporizing liquid in said hydrogenation effluent, the resulting vapors are passed together with hydrogen through an intermediate hydrogenation zone. It is preferable to effect the vaporization of liquid in said initial effluent and separation of the gaseous phase thereof in the presence of a substantial amount of a liquid flux, for example, an amount of flux equal to at least about 5%, and desirably more than about 10%, of said liquid feed. In the intermediate zone, the gaseous mixture is in contact with a porous, solid hydrogenation catalyst having a high hydrogenation activity and a low polymerization activity at a temperature high enough for olefin saturation and also substantially higher than the average temperature in said initial zone under conditions controlled to further hydrogenate said vapors, for example to the extent whereby the diolefin content of the normally liquid fraction thereof is less than about 50%, and preferably less than about 40%, of that of said liquid feed. Next, the effluent is withdrawn from the intermediate zone and passed through a subsequent conversion zone at a temperature suitable for desulfurization in contact with a porous, solid, sulfur-resistant conversion catalyst having at least moderate hydrogenation activity and a high desulfurization activity while controlling conversion conditions in said conversion zone to produce an effluent

with a normally liquid fraction having characteristics exemplified by a Bromine Number less than about 4, and preferably less than about 2, and an organic sulfur content below about 20 p.p.m., and preferably below about 15 p.p.m. In a preferred modification, the temperature at the inlet of the intermediate hydrogenation zone is also high enough for desulfurization.

The aforesaid flux may be any liquid substance or mixture which is miscible with said liquid feed and does not react with it, including immediate reaction products, recycled partially or fully hydrogenated products of the instant process or extraneous liquids, preferably those having a substantial content of aromatic hydrocarbons. The flux may be withdrawn from said vaporization step and from the process in an amount equal to at least about 0.5% (about 1-10% being preferred) of said liquid feed thereby preventing the accumulation of any substantial quantity of polymeric material in the equipment.

Narrower aspects of the invention relate to inhibiting the hydrogenation of aromatic hydrocarbons by the presence of sulfur compounds in the charge to the intermediate zone, specified activity indexes of the various catalysts, the preferred catalysts, operating the intermediate and conversion zones at approximately the same temperatures, locating these two zones in a single reaction vessel and the preferred volumetric ratios of said intermediate and conversion catalysts.

Other narrow embodiments of the invention relate to the selected ranges of the reaction conditions within which the aforesaid control of hydrogenation and conversion reactions is exercised. In the initial zone, these include maintaining a hydrogen partial pressure within the range of about 200-800 pounds per square inch pressure (abbreviated herein as p.s.i.), an hourly space velocity (abbreviated herein as LHSV) within the range of about 0.2-15.0 based on the volume of said liquid feed, a hydrogen charge within the range of about 500-5000 standard cubic feet per barrel of said liquid feed (abbreviated herein as s.c.f./b.) and a feed or charge temperature within the broad range of about 75-300°. Preferred reaction conditions in the initial zone are a hydrogen partial pressure of about 300-600 p.s.i., a space velocity of about 0.5-8.0, a hydrogen charge rate of about 1200-3000 s.c.f./b. and a feed temperature of 75-250° F. For the intermediate zone, they include keeping a hydrogen partial pressure within the range of about 200-800 p.s.i. (about 300-600 being preferred), an hourly space velocity within the range of about 2-60 (preferably about 5-40), a total hydrogen charge within the range of about 500-1000 s.c.f./b. (the preferred range being about 2000-5000), and an inlet temperature within the wide range of about 350-700° (preferably about 400-650°). In said conversion zone, the space velocity may be between about 0.2 and 8.0, and preferably about 0.5-5.0, and the average reaction temperature is not substantially below said inlet temperature of the intermediate zone.

In performing the instant process a feed stock with a pronounced tendency toward undesired polymerization is subjected to a selective hydrogenation process in which it is first hydrogenated mildly in the liquid or mixed phase; the resulting effluent is vaporized under controlled conditions and thereafter treated in the gaseous phase with hydrogen under more severe conditions in at least two catalytic zones. The initial hydrogenation is conducted at a temperature sufficiently low to avoid or minimize both thermal and catalytic polymerization in hydrogenating a substantial portion and usually all or almost all of the diolefins, including all of the more reactive ones, while the catalyst is relatively fresh. During the initial hydrogenation, little, if any, desulfurization is accomplished and a substantial proportion of the monoolefins, often remains unsaturated here as, under some conditions, a more severe hydrogenation at this stage would produce substantial polymerization.

By reason of the stabilizing effect of the partial hydrogenation, most of the initial effluent can now be vaporized without depositing polymeric solids on the equipment, if the vaporization is accomplished by heating in a carefully controlled manner up until the liquid and gaseous phases are separated from one another completely and rapidly in an enlarged separation zone. It is to be noted that the hydrocarbon vapor phase is sharply and completely separated for the first time from the circulating flux liquid including the unvaporized fraction of the effluent by removal of the vapor phase and not by evaporating the liquid phase to dryness or a close approach to dryness.

This gaseous phase is further heated without any further special precautions to a temperature suitable for olefin saturation at a high reaction rate and usually within the range of desulfurization temperatures; then it is subjected to at least two more catalytic treatments with hydrogen at distinctly higher temperatures than in the initial hydrogenation. In the final conversion, the saturation of all remaining mono-olefins and diolefins is substantially completed and organic sulfur compounds are converted into hydrogen sulfide without any appreciable polymer formation occurring in either the preliminary heating or in the vapor phase reaction even though the desulfurization catalyst is customarily of a type of high polymerization potential. The usual difficulties with polymerization are not encountered in this stage because of the earlier hydrogenation of the more reactive diolefins.

When the catalyst in the initial reactor is in relatively fresh condition, most of the hydrogenation of mono-olefins (often more than 80%), as well as diolefins, occurs there. So little hydrogenation of the hydrocarbons occurs in the subsequent reactor or reactors that the exotherms there are quite small with little temperature difference being noted between the inlets and outlets. Eventually as the activity of the catalyst in the first reactor decreases with continued use, more of the hydrogenation load is shifted to the intermediate hydrogenation catalyst bed in the second reactor and substantial increases between the inlet and outlet temperatures of this reactor are then apparent.

This shift of the hydrogenation load demonstrates important advantages of the novel process. In the absence of an intermediate catalyst of high hydrogenation activity operating at a temperature higher than the initial zone, appreciable proportions of fairly reactive unsaturates, including some diolefins, would reach the desulfurization catalyst much earlier than in the present process and deactivate this catalyst sooner by depositing solids thereon. Accordingly, the present invention enables the desulfurization catalyst to remain on-stream for longer periods before regeneration is required to restore its catalytic activity to the necessary level. Similarly, the new method permits the initial hydrogenation catalyst to be kept on-stream for unusually long periods; for with the intermediate catalyst taking up part of the hydrogenation operation, the initial catalyst can be run to a lower level of activity before regeneration without contaminating the desulfurization catalyst with a charge containing excessively reactive hydrocarbons.

The present multistage hydrogenation, in its preferred three-stage form, is not equivalent to a mere extension into an additional stage of either the initial hydrogenation catalyst bed or the final desulfurizing bed of any known two-stage hydrogen treatment. The average reaction temperature is substantially higher, usually at least about 200-500° higher, in the intermediate zone than in the initial hydrogenation zone and a higher heat level substantially increases the hydrogenating activity of the catalyst; hence, some unsaturated aliphatic hydrocarbons of less reactive nature are saturated in the intermediate zone which would not react with hydrogen to any substantial extent at the lower temperature in a first zone of extended size. Also, the intermediate catalyst has a dis-

tinctly higher hydrogenation potential at any given temperature than the desulfurization catalyst, so increasing the size of the desulfurization catalyst bed would not produce comparable results; and this is true even when the intermediate catalyst and the desulfurization agent are located in beds adjacent to one another in the reactor and operating at about the same average temperature.

While it is preferred to locate both the intermediate hydrogenation catalyst bed and the final conversion or desulfurization catalyst in the same reactor for purposes of simplicity and economy, this is not essential and the two catalysts may be located in two or more different reactors. Whether located in the same or separate reactors, the two beds may be operated at about the same average reaction temperature. Little, if anything, appears to be gained by either heating or cooling the gaseous stream between these two stages. Exothermic heat is generated in the final conversion catalyst, usually to a small extent, so that the average temperature at this stage may be slightly above that of the effluent of the intermediate hydrogenation zone. However, in some cases the loss of heat through the reactor walls may exceed the exotherm and result in a final catalyst bed slightly cooler than the intermediate hydrogenation catalyst bed. The ratios of catalyst volume in the intermediate bed to catalyst volume in the final conversion bed generally range between about 1:40 and 1:2.

The arithmetic average reaction temperature in the initial hydrogenation reactor usually runs about 20 to 80° above the temperature of the charge entering the reactor. In the intermediate hydrogenation zone, the reaction temperature is usually found to average between about 10 and 70° above the temperature at its inlet. The average reaction temperature of the final conversion or desulfurization catalyst zone is about the same as the temperature of the charge entering there. To mention a few typical figures, the average temperature of the initial hydrogenation bed may be about 125° F. for palladium, about 200 for platinum and about 230 for a nickel catalyst; and for the intermediate hydrogenation zone, the average temperature for the same three catalysts may be about 375, 400 and 425°, respectively. When the desulfurization catalyst comprises the oxides or sulfides on cobalt and molybdenum on an alumina support, the average temperature in the final catalytic zone may be about 350–700 and preferably about 400–650°.

As the starting material, any mixture of aromatic and unsaturated aliphatic hydrocarbons with organic sulfur compounds may be employed in the present process if the final boiling point of the liquid does not exceed about 500°. A narrow boiling range material, for example, one having a boiling range between about 140 and 275°, is desirable and preferably a charging stock boiling in the range of about 160 to 220° for producing benzene.

As a source of aromatic hydrocarbons, the liquid feed desirably contains a total of between about 20 and 90% aromatics, especially benzene and toluene. Typically, it also has substantial contents of diolefins and olefins as evidenced by Diene Numbers of about 10 to 25, which measure the proportion of conjugated diolefin 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 somewhat higher than about 45 and about 75 respectively may also be processed according to the present invention. The organic sulfur content is typically about 20 to 300 p.p.m. and may be as high as about 1000 p.p.m.

In other utilizations of the present process, the charging stock need not be rich in aromatic hydrocarbons. For instance, in producing a stable gasoline blending stock from a pyrolysis liquid, a feed containing 6 to 20% aromatic compounds is typical.

Feed stocks 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 into the present process. In addition it is recommended that the liquid feed 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. This prolongs the activity of the catalysts usable in this process. Such feed stocks are generally obtainable by severely thermally cracking a petroleum fraction suitable for the manufacture of gasoline or light olefins as exemplified by ethylene. It is preferred here to depentanize the cracked product. A particularly preferred feed is one with an end point not exceeding 220° and a maximum gum content of less than 15 milligrams per 100 milliliters.

The total consumption of hydrogen in this process varies of course with the particular feed stock employed, but in general, it is in the range of about 150–900 s.c.f./b. of liquid feed stock. A typical value is 300 s.c.f./b. with a charging stock of Diene and Bromine Numbers of 15 and 24 respectively. The consumption is usually found to be less than 500 s.c.f./b. Substantial excesses of hydrogen have been specified hereinbefore to maintain a sufficient hydrogen partial pressure to avoid a drop in the degree of hydrogenation. 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 or hydrodesulfurizing gas oils, etc. The gas charge preferably has a hydrogen content of at least 60% but gaseous mixtures with as little as 40% hydrogen may be used, such contents referring to percent by volume or molar percent.

The partial pressure of hydrogen in the two or more reactors is important in avoiding undesired side reactions, such as the formation of gum or coke on the catalysts. It should be maintained within the range of about 200–800 p.s.i., the 300–600 p.s.i. range being preferred. The total pressure in the reactors is not critical but it should not be so high as to interfere significantly with the vaporization of the feed and reaction products described herein. Typically, a major proportion of the product gases with much unconsumed hydrogen is recycled to the process after any excessive quantities of hydrogen sulfide have been scrubbed out and this usually constitutes a major proportion of the total quantity of gases charged to the reactors.

The charging stream of combined recycle and make-up gases containing hydrogen is divided into several streams. A substantial quantity of hydrogen must be introduced into the first reaction zone along with the liquid feed, and unreacted hydrogen is present in the effluent of that reaction which is subjected to further hydrogenation reactions. While in theory all of the hydrogen-rich gas required for the series of selective hydrogenations can be charged to the initial reactor, this is not particularly desirable in practice. Especially since the circulating gas may be employed after heating to a high temperature in a furnace as a heat source to aid in vaporizing the effluent from the initial reactor and also to regulate the temperature of the vapor phase charge of hydrocarbons and hydrogen to a subsequent reactor. Alone this hydrogen-rich gas stream can be heated without decomposition or other difficulty to a temperature several hundred degrees higher than it is possible to heat the liquid or mixed phase effluent of the first reactor without the coincident deposition of polymeric gum or coke. Such deposition from the mixed phases can occur at temperatures of 300° or even lower. In serving as a heat source, a substantial part of the total circulating gas, say about 30 to 85%, is heated to a temperature in the range of about 500 to 950°, and preferably in the range of about 600–850°, while the unheated balance of the gas is charged to the initial reactor. One stream typically containing more than half of this heated gas is used to supply the final temperature increment to the initial mixed phase effluent just prior to entering the enlarged separating and vaporizing chamber and the re-

mainder may be introduced into the wholly gaseous stream leaving the top of said chamber on its way to the second stage reactor as the final heat increment to adjust the charge to the desired inlet temperature.

A catalyst of high hydrogenation activity is required for the initial reaction zone as it must hydrogenate at a relatively low temperature the more reactive conjugated diolefins and usually at least some of the other olefins, but the polymerization activity of this catalyst must be relatively low in order to avoid the formation of gums which will deactivate it. While some suitable hydrogenation catalysts also incidentally possess relatively high desulfurization activity initially, this property usually drops off rapidly in a period of a few days to a week, because such catalysts are readily poisoned with respect to desulfurizing ability at desulfurizing temperatures by feeds containing much organic sulfur.

These qualities of the catalysts may be defined in terms of arbitrary activity indexes which are described herein. Unless otherwise stated, all such indexes are measured using fresh new catalyst. The activity indexes enable one to clearly differentiate between the two or more catalysts employed at various stages in the instant process.

For delineating hydrogenating activity, two different indexes are available. The hydrogenation activity index is defined herein as the percentage or proportion of isoprene which is converted to pentenes and pentanes when a blend of 8-10% isoprene and 50-500 p.p.m. of thiophene sulfur in benzene is passed over the catalyst with 1500-3000 s.c.f./b. of hydrogen gas at 150° F., 300 pounds per square inch gage (hereinafter designated p.s.i.g.) as the total pressure and a liquid hourly space velocity of 5. Thus a conversion of half of the isoprene present, or 4.5% out of a total of 9.0% isoprene present, signifies that the activity index is 50. For the initial and intermediate zone catalysts, a hydrogenation activity index of at least about 40 is recommended.

In determining the benzene conversion index as another and usually supplemental measure of hydrogenation activity, a sulfur-free mixture of 17% benzene and 83% cyclohexane is passed through the catalyst under test at 400° F. and 400 p.s.i.g. with 1500-3000 s.c.f./b. hydrogen circulation and a liquid hourly volumetric space velocity of 2. The test mixture must be sulfur-free inasmuch as organic sulfur in a content as small as 50 p.p.m. and even less in the form of hydrogen sulfide, totally inhibits the hydrogenation of benzene with many catalysts under the specified reaction conditions. A suitable catalyst for the initial and intermediate zones has a benzene conversion index of at least about 50, meaning that half of the benzene present or 8.5% is converted into cyclohexane, but an index of about 100 is typical for the preferred catalysts.

Another means for designating suitable catalysts for the first and intermediate zones is the polymerization activity index. This is another arbitrary index which equals the percentage of isoprene that is polymerized when 25 cc. of a mixture of 8-10% isoprene in benzene is heated with 5 cc. of the catalyst to be tested in a stationary bomb of 30-55 cc. capacity to a temperature of 350° under a blanket of inert nitrogen gas and held there for one hour. The polymer formed from the isoprene remains on the catalyst, or the interior surface of the bomb and the liquid consisting of benzene and unreacted isoprene is poured off and analyzed chromatographically. The decrease in isoprene monomer due to polymerization is calculated by difference between the isoprene content of the reaction product and that of the test blend charged. A satisfactory catalyst for the initial and intermediate stages has a polymerization activity index less than about 35, as polymerization there is undesirable.

An arbitrary desulfurization activity index may also be used in the present invention, principally for determining suitable catalysts for the subsequent desulfuriza-

tion operation. This index is the percent reduction in sulfur content obtained when a blend of pure compounds consisting of 10% hexene and 10% isoprene in 80 volume percent of benzene with a total thiophene sulfur content of 500 p.p.m. is passed over the catalyst in question at 500° F. and 450 p.s.i.g. together with between 1500 and 4000 s.c.f./b. of hydrogen at a liquid hourly volumetric space velocity of 2. For suitable desulfurization, the final stage catalyst desirably has a desulfurization activity index of at least about 80, both fresh and after one week of operating with the test feed stock. It has been observed that many good catalysts for the initial hydrogenation zone also have desulfurization indexes in the 80-100 range initially, but usually these catalysts are quickly poisoned or deactivated by a sulfur content equivalent to that in the test feed so that after one week of operation the activity index is in the 0 to 50 range.

Catalysts of substantial acid activity are usually not desirable for the initial and intermediate stages of this process since they produce unwanted cracking reactions, so silica-alumina catalyst supports are usually avoided. However, 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. Furthermore, a catalyst is favored which is substantially devoid of alkylation activity and thus does not promote the alkylation of aromatics with olefins.

Although they are not necessary, porous particle form supports are recommended for all of the catalysts used in the instant invention to adequately disperse and increase the surface area of the actual catalytic agent. In the case of expensive agents such as platinum, the support is quite important from an economic standpoint in commercial-scale operations. The particle form support may take the physical form of pellets, rods, tables, spheres or granules of irregular shape. The average particle size may range from $\frac{1}{16}$ inch to $\frac{1}{2}$ inch.

The porous supports may take the form of natural or treated clays, such as Fuller's earth, kaolin, bentonite, montmorillonite and superfiltrol; treated clay-like materials, such as celite and sil-o-cel; artificially prepared or synthetic materials, such as magnesium oxide, silica gel alumina gel, and the like; or the zeolites, activated carbon, diatomaceous earth, kieselguhr, infusorial earth and the like. Adsorptive aluminas, bauxite or porocel are particularly desirable carrier materials. Activated alumina, a well-known crystalline alpha alumina monohydrate prepared by partial dehydration of crystalline alpha alumina trihydrate, is very satisfactory for the purpose. Another highly satisfactory form of alumina is currently marketed by the Aluminum Corporation of America under the name F-10 Alumina. F-10 Alumina is chi alumina prepared by the precipitation of alpha alumina trihydrate from an aluminate solution below 140° F. After filtering and drying, this material is calcined first between 536 and 842° F. to effect partial dehydration, and later at 750 to 1470°.

A variety of catalyst of differing chemical constitution may be employed in the initial and intermediate hydrogenation steps as long as they have the necessary activity described herein. Platinum in amounts ranging from about 0.05 to 2.0%, preferably about 0.2-1.0%, supported on various aluminas and especially gamma and chi alumina, is suitable as are the other noble materials in Group VIII of the Periodic Table of Elements with atomic numbers of at least 27, such as rhodium and palladium. The concentration of palladium in such catalysts may be about 0.05-10% and about 0.2-2.0% is preferred for the purpose. Within the latter limits, the hydrogenation activity of the catalyst increases when the palladium content is increased. Nickel, either unsupported or on unknown supporting materials in concentrations ranging down to about 10% nickel in the composite catalyst also provides satisfactory results, as

does copper chromite. For instance, good hydrogenating characteristics for the first reactor are obtained with 55% nickel supported on kieselguhr—a composite that is strongly selective in hydrogenating diolefins in preference to olefins. By reason of their high hydrogenation activity at low temperature, palladium or platinum on gamma alumina are recommended, palladium being preferred for the initial reaction, since its greater activity catalyzes the desired hydrogenation reactions at a temperature about 100° lower than in the case of platinum. The palladium composite is desirably promoted in some instances with a quantity of chromia in the same range as the palladium. Platinum on a support of alumina or another suitable material is preferred for the intermediate reaction stage because of its apparently superior resistance to the higher temperatures in that zone. Among the many suitable specific catalysts are 5% palladium on activated carbon and 0.6% platinum on eta or chi alumina of less than 0.01% chlorine content. The manufacture of such catalysts is well known in the art and accordingly is not described here.

The catalysts employed in the second and any subsequent reactor operate under quite different reaction conditions from those in the initial reactor. The charge is entirely in the gaseous phase and the temperatures employed are substantially higher than in the initial hydrogenation zone. As a result of the substantially greater average temperature in the intermediate catalyst bed producing enhanced hydrogenation activity, hydrogenation proceeds there with further saturation of diolefins and usually of a substantial proportion of monoolefins also, even where the feed stock has been partially saturated by a treatment with the same catalyst in the first reaction zone. In the final stage, the reaction products leaving the intermediate catalyst bed are further treated with hydrogen in the presence of a desulfurization catalyst to desulfurize the charge and to substantially complete the hydrogenation of the less reactive unsaturated hydrocarbons therein, namely the monoolefins and any remaining diolefins. The desulfurizing reaction requires a temperature sufficiently high for organic sulfur compounds to be converted into hydrogen sulfide at a commercially acceptable rate or space velocity. With the catalyst commonly employed, this means that the inlet or charge temperature should be at least about 350°, and preferably at least about 400°.

The conversion catalyst in the last reaction stage may be any known desulfurization catalyst including tungsten disulfide, nickel sulfide, nickel-tungsten sulfide and chromia on alumina promoted by molybdena. Combinations of a compound of a metal in Group VI B of the Periodic Table of Elements, for example a chromium, molybdenum or tungsten compound, together with a compound of a metal of the iron group provide good results and it is usually desirable to support such agents on a conventional catalyst support, such as alumina, kieselguhr, etc. The oxides or sulfides, particularly the latter, of cobalt and molybdenum supported on gamma alumina are preferred for the desulfurizing operation. In catalysts of this type the concentration of cobalt may range from about 1 to 5% while that of molybdenum may be between about 5 and 18%.

The final catalyst may also be defined in terms of an arbitrary desulfurization activity index as set forth hereinbefore in the 80–100 range which activity is retained for a period of at least one week and usually much longer. It should also have at least moderate hydrogenation activity. The increased temperature of the final reaction greatly increases the actual hydrogenation activity of these catalysts. Also it has been found that some and perhaps all catalysts which are well suited for the final desulfurization reaction have relatively high polymerization activity indexes exceeding about 25 on the scale defined hereinbefore, even though such activity is

neither directly concerned with nor desired in the instant process. By reason of the prior partial or complete hydrogenation of the more reactive diolefins in the charge to the final stage, there is little tendency for polymerization to occur.

In illustration, the presulfiding or final step in the preparation of a preferred type of desulfurization catalyst comprising sulfides of cobalt and molybdenum on alumina may desirably be performed in situ in the final reactor, provided that any noble metal or other catalyst susceptible to poisoning by hydrogen sulfide is absent from the reactor. Otherwise either the noble metal catalyst should be removed before this operation, or the sulfiding step should be performed elsewhere or the reactor should be purged with a hydrogen-rich gas for at least 10 hours after sulfiding, and preferably about 20 hours, at normal average reaction temperatures. In this illustration, a fresh contact catalyst containing cobalt molybdate on the surface of a suitable support such as gamma alumina or a catalyst regenerated to the oxide state by combustion with air diluted by steam is subjected first to pre-reduction for six hours at 700 p.s.i.g. and 700° with a hydrogen-rich recycle gas substantially free of hydrogen sulfide. Following the prereduction step the catalyst is then contacted with a circulating stream of mixed hydrogen sulfide and hydrogen under conditions such that the minimum partial pressures are 8 p.s.i. for hydrogen sulfide and 100 p.s.i. for hydrogen and the temperature is in the range of 500 to 700°. The treatment is concluded at a temperature of about 700° after being continued until the sulfur content of the composite catalyst rises to the range 6.5–7.5% whereupon the catalyst is ready to be placed on stream. Later during desulfurizing operations under a hydrogen partial pressure of 300 p.s.i. or more, the sulfur in the catalyst drops from that range to an equilibrium content of about 4.6%.

Returning now to the first reactor, suitable ranges of reaction conditions have been described earlier and the actual reaction conditions are selected and regulated within those ranges in a manner known to those skilled in the art to produce an initial hydrogenation effluent in which desirably at least about 35%, and preferably at least 50%, of the original diolefins have been converted into mono-olefins or paraffins and in which an amount equal to at least about 25%, and preferably at least about 80%, of the liquid feed rate remains in the liquid phase. It is also preferred to obtain an effluent liquid fraction with a Bromine Number at least about 25% below that of the liquid feed.

The regulation of such reaction conditions and the effect of one operating variable upon another are well understood by those skilled in the art and need not be explained in detail here. For instance, if the degree of hydrogenation tends to drop below the minimum specified, or perhaps below the preferred values, this condition can be corrected by increasing the feed temperature or decreasing the space velocity or both. Also if the proportion of initial reactor effluent in the liquid phase drops below the minimum specified, the feed temperature may be decreased, the space velocity increased to reduce the total exothermic heat generated and provide a greater quantity of reactants to absorb the heat liberated, or the pressure increased or any combination of these measures may be employed in reducing the degree of vaporization in the initial reactor. Using the same circulating gas, an increase in total pressures of course results in a corresponding increase in hydrogen partial pressure.

With a fresh catalyst, either new or regenerated, it is obviously most economical to maintain the feed or charging temperature at the lowest temperature at which the gaseous and liquid components of the charge are readily available thus avoiding any heating or cooling expense and minimizing gum formation. The feed temperature is desirably within the stated range and, in the preferred operation, the feed temperature is maintained at a sub-

stantially constant value within the narrow range of 75–190° F., in the lower part of that range being recommended, while the catalyst is fresh. Usually, this temperature is subsequently increased either gradually or by steps but not beyond about 300° F. in order to maintain a diolefin reduction of at least 35%, and preferably to maintain a substantially constant degree of saturation, as the hydrogenation activity of the catalyst decreases with continued use. Even with a fresh catalyst, the first hydrogen treatment customarily does not fully saturate all of the olefinic or unsaturated aliphatic compounds for the Bromine Number reduction usually is in the range of about 25–95%.

Regeneration of the initial hydrogenation zone catalyst is recommended when the Diene Number reduction is less than 35%, or the degree of vaporization exceeds 80%, or both, after the feed temperature has been adjusted upward to the maximum temperature that is considered suitable for the particular catalyst. These are better criteria than prescribing a maximum outlet temperature for the initial reactor inasmuch as the degree of vaporization of the effluent and the degree of saturation of its more reactive original components, are more significant than the outlet temperature in the instant process. In addition, it appears that the maximum permissible outlet temperature can vary considerably for different feed stocks over the range of about 275 to 400°. For instance, a reactor outlet temperature of 325° is considered excessive for certain low boiling feed stocks but will give satisfactory results with other feeds boiling at higher temperatures ranging up to end points near 500°.

It is further apparent that an attempt to define acceptable outlet temperatures is not feasible in consideration of the variations in permissible pressures in the reactor. For example, an outlet temperature of 325° would be suitable for a relatively high reaction pressure in retaining the desired proportion of effluent in the liquid phase while a lower temperature would be necessary if the minimum pressure were employed while all other conditions were held constant. Thus, as a result of the close interrelation of the various operating conditions, it is more significant to describe a preferred embodiment of the initial hydrogenation in terms of the regulation of certain reaction conditions within restricted ranges to provide an intermediate product in which a certain proportion is retained in the liquid phase and a certain amount of the more reactive feed components are at least partially saturated.

An entirely different situation prevails at the outlet of the desulfurization reaction zone as it is unlikely that any exotherm created by the reaction conditions mentioned herein can reach a temperature sufficiently high to deactivate the catalyst. However, to permit the use of ordinary construction materials, the maximum outlet temperature should not exceed about 850°.

Although catalysts in the form of palladium or platinum supported on alumina retain sufficient activity for extremely long periods, as for instance, 5 months and usually more in the case of palladium catalysts, regeneration of the catalyst is eventually necessary. This may be readily accomplished by heating the reactor to a temperature of about 700–900° for a palladium-alumina bed while passing a gas containing 1 to 2% oxygen there-through. A diluent is usually introduced with the air to avoid excessive regeneration temperatures which can reduce catalyst activity considerably. Nitrogen or flue gas may be used generally for that purpose and the more convenient medium of steam may be utilized as the diluent with a palladium catalyst. The regeneration of other hydrogenation catalysts suitable for use in the initial or intermediate stages of the novel process may also be performed by known methods.

The desulfurization or final stage catalyst is conventionally regenerated in similar fashion at even longer intervals of about 9 months or more when the organic

sulfur content of the final reactor effluent exceeds 20 p.p.m. even when the inlet temperature of that reactor has been raised to the permissible maximum. This regeneration converts most of the cobalt and molybdenum compounds to oxides and a presulfiding treatment such as the one described hereinbefore is preferably employed to restore the catalyst to its original more active sulfide form.

It has also been found that purging the initial and intermediate contact masses with hydrogen at 200–500 p.s.i.a. and 750–850° for 16–4 hours sometimes serves to regenerate certain catalysts, such as palladium, almost as effectively as conventional regeneration by combustion with air diluted to an oxygen content of 1 or 2 percent. Accordingly, it is contemplated that, in the absence of severe deactivation of the catalyst, these catalysts may be regenerated several times by such treatment with hydrogen-rich gas before it is necessary to regenerate them by the combustion technique.

Only a limited amount of hydrogen sulfide may be tolerated without substantial deactivation by certain of the catalysts suitable for the first and intermediate reaction stages. Although this loss of activity may be readily restored either by regeneration of the catalyst in the usual fashion or the hot hydrogen treatment described earlier, frequent regenerations reduce the over-all efficiency of the process. Accordingly, in the case of a platinum catalyst supported on alumina, it is desirable that the partial pressure of hydrogen sulfide in the gaseous phase should not exceed 0.05 p.s.i. and preferably should be less than 0.03 p.s.i. The effect on a palladium catalyst is similar. Organic sulfur generally has a lesser effect on the catalyst and it is a relatively simple matter to control the hydrogen sulfide which is introduced in the hydrogen-containing gas by simply passing either or both of the make-up and recycle gases through an alkaline scrubber, or other unit for removing hydrogen sulfide such as a diethylamine absorber.

Under severe conversion conditions, for example a high desulfurization temperature in combination with a low space velocity of perhaps less than 1, a sulfided composite of cobalt and molybdenum on alumina may catalyze the hydrogenation of a part of the aromatic hydrocarbons, as exemplified by the conversion of benzene to cyclohexane. This is usually undesirable and may be easily avoided by inhibiting the reaction by maintaining a concentration of sulfur compounds in the charge equivalent to inhibiting effect to at least about 50 p.p.m. of thiophene sulfur (e.g., about 20 p.p.m. of hydrogen sulfide). The intermediate hydrogenation catalyst may produce the same unwanted type of reaction and probably to a greater extent under similarly severe conversion conditions, and the same inhibiting treatment is useful in this zone also. Where the charge contains less of such sulfur compounds it is a simple matter to supply additional hydrogen sulfide in the hydrogen-rich gas which is introduced upstream of the final reactor. Selection of a make-up gas of suitable hydrogen sulfide content or by-passing the recycle gas around the caustic soda scrubber are some of the methods useful in attaining any additional inhibiting effect.

Despite the unstable nature of the hydrocarbon feed stock, very little if any gum is formed in the first reactor. The relatively low reaction temperature is not conducive to thermal polymerization. A catalyst having little or no polymerization activity is employed. A substantial proportion of the reaction mixture is maintained in the liquid phase to avoid approaching the point of dryness in the reactor. 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 second catalytic reaction with hydrogen is entirely a vapor phase operation; hence, it is necessary to vaporize most of the effluent of the first reactor. Accom-

plishing this by merely passing the initial effluent through a heater and into a second reactor is not satisfactory even though this technique has been suggested in the prior art. Such procedure deposits polymer either in the heater or in the next catalyst mass or both, and stoppages of this nature call for much cleaning and/or regeneration that reduce the overall operating efficiency. Accordingly, vaporization of the initial effluent in the presence of a flux liquid is preferably employed here. This may be accomplished by various methods, one of which involves a combination of stages in which the initial hydrogenation effluent is gradually heated under good temperature control in the presence of a flux, preferably circulating in substantial quantity through the transfer line between the initial reactor and a vaporizing and separating chamber of enlarged cross section. In that chamber vaporization of the initial original feed and products thereof is completed to the desired extent of about 90 to 99% and seldom more than 99.5%. The small but significant balance of unvaporized effluent is withdrawn at least intermittently from the process as a liquid leaving the enlarged chamber and it carries a small amount of polymer formed during the vaporization operation and possibly also in the initial hydrogenation step or perhaps present in the original charge stock. Once this separation of the gaseous and liquid phases has been accomplished, there is no longer a tendency toward any significant polymerization in the gaseous phase containing the major proportion of the hydrocarbons even when it is heated up to temperatures of 350 to 700 which would have produced an unacceptable degree of polymerization in the mixed phase material from the initial reactor.

The gradual heating of the initial effluent to effect controlled vaporization during passage of the effluent through the restricted transfer conduit (including heater passages, etc.) leading from the initial reactor to the vaporizing and separating chamber may be accomplished by several means. One, comprises an optional but preferred technique in which a circulating liquid flux at a substantially higher temperature, than the effluent typically of the order of 75–200° higher, is injected into the initial hydrogenation effluent near the outlet of the first reactor. It will be appreciated that the exotherm of the initial reaction has already increased the temperature of this effluent substantially above the temperature of the feed to that reactor. The temperature of the mixture of flux and reaction effluent is preferably increased further during passage through an indirect heater which is desirably heated with steam or another easily controllable medium for even heating. A relatively low temperature difference between the heating and the heated media is highly desirable to provide the gentle heating that minimizes polymerization in such equipment. Indirect heat exchange is recommended for the major heat input into the stream passing through the transfer conduit. Finally, and preferably closely adjacent to the inlet of the separator pot, an additional stream of the hydrogen-rich gas used in this process may be injected into the mixture at a substantially higher temperature up to several hundred degrees higher than the temperature of the mixture. This direct contact heating with jet of hot gases is an optional but highly desirable feature which minimizes polymer deposition on equipment surfaces. With each of these increments of heat, more of the first reactor effluent is converted in the transfer conduit from the liquid phase into the gaseous state under conditions in which the presence at all times of a substantial liquid phase assists in preventing or at least in minimizing the deposition of polymeric material on heated surfaces. The enlarged cross section of the chamber provides good conditions for separating the two phases by reducing the vapor velocity sufficiently so that all of the liquid drops out of the rising gaseous phase.

The supply of steam to the indirect heater may be manually controlled to maintain a predetermined tempera-

ture in the separating chamber as steady as possible, but better results are usually obtainable in regulating the steam supply in response to the liquid level in the separating chamber. That regulating system involves controlling the input of steam manually, but preferably automatically, in direct response to the signals of a conventional liquid level indicator or controller attached to the vaporizing and separating chamber. The removal of liquid streams from that chamber as well as any input of external flux is desirably maintained at constant flow rates under the regulation of automatic flow controllers; therefore, a rise in the liquid level in the separating chamber represents a decrease in the vaporization of the initial hydrogenation effluent and a fall in that level means that the effluent is being vaporized in a greater degree. To maintain a steady degree of vaporization more steam or less steam respectively is supplied to the indirect heater. The heating steam may be adjusted by means of a valve in the steam supply line or one in the line used for draining condensed heating steam from the heater.

Conventionally, control of vaporization of a generally similar nature is regulated in response to the temperature of the vapor or perhaps the liquid temperature. Such control is subject to the usual deviations encountered in efforts to obtain precise elevated temperature measurements that arise from radiation or evaporation of liquid on a temperature sensing element, etc. Moreover, it is not particularly satisfactory for liquids of narrow boiling range, such as the preferred feeds of the present invention, inasmuch as a small temperature differential of only a few degrees at a substantially elevated temperature generally is related to a large differential in the proportion of liquid vaporized. Thus control of heating of the liquid in direct response to the actual proportion of unreacted feed stock plus reaction products (initial effluent) retained in the liquid phase is much simpler and far more accurate here than control based on the indirect factor of temperature which is further influenced by variations in pressure, in the composition of the liquid, in hydrogen to liquid feed ratios and system lag.

Either manual or automatic control of the heating of the initial effluent in direct response to the liquid level in the flash chamber may also be extended to controlling the quantity of heat supplied by the stream of hot hydrogen-rich gas injected into the transfer line near the inlet of the separator pot. This regulation may govern either the quantity of said gas being admitted to the transfer line or the temperature at the charge outlet of the furnace described hereinafter for heating that gas. Also, it is possible to control both the heat input to the indirect heater through which the initial effluent passes and the heat furnished to the effluent by the hot hydrogen-rich stream in response to the liquid level controller on the vaporizing and separating chamber. However, it is usually preferred from a standpoint of practical operations to apply such regulation only to the steam input to the indirect heater.

The flux liquid comprising the liquid fraction of the effluent from the initial reactor and any inert liquid miscible therewith that is introduced into the transfer line may perform several functions before being separated from the gaseous portion of that effluent in the separation chamber. It minimizes or inhibits gum formation at this critical stage of the preferred process wherein a stream of mixed gaseous and liquid hydrocarbons containing gum-forming precursors is carried to a relatively high degree of vaporization by heating, for the flux prevents the effluent from approaching dryness too closely, for example, not closer than about 5% based on the original liquid feed rate. Secondly, the circulating flux serves as an economical and relatively gentle direct heating medium for vaporizing a portion of the initial effluent. Finally, the flux liquid prevents, or at least minimizes the deposition of any gums or polymeric solids on the pipes and other apparatus by reason of its washing action on

the surfaces thereof and its solvent characteristics which enable it to retain in solution any polymeric material whether formed at this stage or earlier.

Although any hydrocarbon liquid of suitable boiling and stability characteristics may be employed as the flux, it is preferred that the content of aromatic compounds should amount to at least 15% to improve its capability for dissolving gummy material. A flux liquid from an external source may be used, and it is suggested that its volatility should be sufficiently low that a major proportion and preferably substantially all of the flux remains in the liquid state under the conditions in the vaporizing chamber while its resistance to coking and polymerization should desirably be at least as good as that of the initial effluent. Its boiling range is preferably located between about the boiling point of benzene and about 950°. However, an economical and readily available flux liquid may be obtained very simply by merely reducing the heating in the transfer line between the first reactor and separator at the start of a run in order to retain a larger than usual proportion of the initial reactor effluent in the liquid phase until a sufficient body of flux liquid has been built up in the system. This of course amounts to accumulating the least volatile fraction of the feed stock as the liquid flux.

The rate of recirculating the flux liquid may amount to at least 5%, and preferably at least 10%, of the rate of introducing the liquid feed stock into the first reactor, and lesser amounts may be recirculated where an appreciable proportion of the initial effluent is retained in the liquid phase throughout the vaporizing step. As used herein, all flux (liquid effluent plus any added liquid) quantities or rates relate to the proportions at the moment when the maximum degree of vaporization of the initial effluent is attained; and, of course, the proportion of material in the liquid phase reaches its minimum—namely the instant of separation of the gaseous and liquid phases—rather than at the confluence of a circulating flux stream with the initial hydrogenation effluent. Much higher flux circulating rates can be employed ranging up to 40%, and even to 200% or more, for the only real limitations are physical ones relating to the capacities of the equipment and economic ones relating to pumping costs and the cost of larger equipment. When the total proportion of liquid in the transfer line and heater is ample by a substantial margin to avoid dryness and bathe the walls of the equipment, further increases in the flux circulation rate do not achieve a corresponding or even a significant reduction in the amount of polymer formed in the system or even in the polymer concentrations in the flux liquid; hence, high circulation rates provide no important advantages.

The concentration of polymer in the circulating flux is dependent on the quantity of spent flux withdrawn from the vaporizing step and from the instant process either intermittently or preferably continuously. This spent liquid is derived from an unvaporized fraction of the effluent of the initial reactor or from a supply of external flux or from both sources, and over any substantial period the rate of withdrawal must equal the supply from these sources. Under the preferred steady state conditions, reducing the degree of vaporization of the initial effluent and correspondingly increasing the spent flux withdrawal results in a decrease in the polymer concentration in the circulating flux and vice-versa. As indicated earlier, this removal of spent flux liquid amounts to at least about 0.5%, and desirably about 1 to 10%, based on the liquid feed rate. While the amount may be larger, it is generally uneconomical to withdraw much more in the liquid phase for purification or further processing. In actual practice a flow controller on the spent flux line from the vaporizing chamber may be adjusted manually as needed to keep the gum content of the circulating liquid low enough to avoid the deposition of polymeric material in the equipment; for example,

by keeping the gum content below about 200 milligrams per 100 milliliters.

Where a flux liquid from an external source is supplied to the system at a constant and usually relatively low rate, it is possible to vaporize a correspondingly greater proportion, in fact the whole of the liquid effluent fraction of the first reactor. However, it is preferable to retain the least volatile 0.5 or 1% of said effluent in the liquid state in order to keep the temperature as low as possible during the vaporizing operation. For example, with all percentages based on the liquid feed rate, one may continually charge 5% of a hydrocarbon oil having an atmospheric boiling range of 600-700° and a major proportion of aromatic hydrocarbons to the separating chamber as circulating flux, and recycle 25% liquid from this pot to the transfer line immediately downstream of the first reactor; then vaporization of the effluent-flux mixture in the transfer line may be controlled by appropriate heating to retain 1% of the initial effluent in the liquid phase in that chamber and 6% spent flux may be withdrawn continually from the bottom thereof in maintaining steady operations.

The size and shape of the separating and vaporizing chamber are not critical. In avoiding or minimizing appreciable entrainment of liquid droplets in the vaporous phase that is leaving, it is desirable to keep the velocity of the gaseous phase relatively low, perhaps 2 feet per second or less. This can be achieved by providing a reasonably large cross-sectional area perpendicular to the direction of gas flow in the upper part of the vessel. On the other hand, where the heat for vaporization is regulated in response to liquid level in the chamber, it is desirable to have a relatively small cross-sectional area in the neighborhood of that level in order that a significant change in level will occur whenever a significant change in the degree of vaporization of initial effluent occurs. Such factors pose no great problems, as there is no necessity for maintaining a constant cross-sectional area throughout the length of the chamber. As one illustration, the vessel may be in the general form of a double cylinder having a lower section of considerably smaller diameter than the upper section.

After separation of the flux liquid from gaseous material derived from the effluent of the initial reactor, this gaseous phase is heated to bring its temperature up to the desired inlet temperature of the second reactor and its proportion of hydrogen is boosted, if necessary, to the desired level for that reactor by the introduction of a hydrogen-rich gas. These steps may be combined, if so desired, by introducing the extra hydrogen-containing gas at a substantially greater temperature, say about 100° to 400° more, than that of the gaseous phase leaving the separating chamber. This is one of the suitable methods of making the final temperature adjustment in the charge to the second reactor. It is preferably accomplished by regulating the volume of fuel gas burning in a furnace for heating circulating gas and consequently the outlet temperature of that circulating gas stream either manually or automatically in response to signals from a temperature sensing device located in the conduit leading to the inlet of the second reactor.

For a better understanding of the nature and objects of this invention, reference should be had to the detailed description and examples hereinafter taken in conjunction with the accompanying drawing which is a simplified flow sheet or schematic representation of the process of the present invention. It will be appreciated that many details well known to petroleum engineers have been omitted from the drawing or simplified for simplicity and greater clarity including pumps, valves, alternate and parallel piping and equipment and control equipment, especially instruments for indicating, recording or regulating temperature, pressure, level, flow, etc.

Turning now to the drawing, a freshly-distilled stream of thermally cracked and depentanized gasoline (160–220° B. R.) of the composition set forth in part in column 1 of Table I hereinafter enters the feed conduit 2 at ambient temperature and a pressure of 740 p.s.i.g. at the rate of 2300 b./d. This narrow cut is substantially free from two easily polymerizable and therefore particularly troublesome compounds, namely cyclopentadiene which boils about 106° and styrene which boils around 293°. A fresh or make-up gas rich in hydrogen and obtained from the off-gas of a conventional unit for catalytically hydrodesulfurizing gas oil is admitted in pipe 4 at a pressure of 750 p.s.i.g. The quantity and composition of this gas are specified in column 2 of Table I. This make-up gas joins the recycle gas stream, which is described later, in conduit 6. The resulting mixture has a temperature of 125° F. and its composition and rate of flow are designated in column 3 of the table.

Half of the mixed gas stream in conduit 6 is taken off in the valved line 8 for purposes that will be apparent later. The other half of the gaseous material continues to travel along pipe 6 until it joins the pyrolysis liquid hydrocarbons in conduit 2, and this gas-liquid mixture of the composition and flow rate given in column 4 of Table I passes through the heater 10 where its temperature is adjusted to 115° (herein designated as the feed temperature) by heating, if necessary, on its way to reactor 12. This charge temperature produces good results with the catalyst described hereinafter which has been partially deactivated in service.

Column 4 of Table I sets forth the total charge to the first or initial reactor 12 which contains a fixed or stationary catalytic bed 13 of chromia-promoted palladium on a gamma alumina support in the form of $\frac{3}{16}$ " diameter cylinders $\frac{3}{16}$ " long. Based on the total weight, there is a surface deposit on the alumina of 0.50 percent of palladium metal and also 0.51 percent of chromium in the form of oxides.

The reaction conditions in the first reactor 12 are:

Inlet temperature	-----° F--	115
Outlet temperature	-----° F--	170
Pressure	-----p.s.i.g--	730
Hydrogen partial pressure (inlet)	-----p.s.i--	450
H ₂ :liquid feed charging ratio	-----s.c.f./B--	1900
Liquid space velocity	-----v./hr./v--	2.2
Catalyst Activity Indexes		
Hydrogenation	-----	100
Polymerization	-----	<22
Desulfurization	-----	0

In the first stage reaction the primary reaction is one of the nondestructive hydrogenation of diolefins, especially conjugated diolefins, accompanied by considerably less saturation of the less reactive mono-olefins. The temperatures are below the level required for desulfurization and no significant hydrogenation of aromatics or polymerization takes place there.

Any trace of gum formed in the catalyst bed dissolves in the descending liquid and the reaction effluent is drawn off at the bottom of the reactor via conduit 14 in which it is transported to heater 15. A minor portion of the liquid feed stock or reaction products thereof vaporizes in reactor 12 as a result of the heat evolved in the exothermic hydrogenation reaction.

A circulating flux liquid at 350° is injected from the conduit 16 into the products in pipe 14 partly to increase the temperature of the initial reactor effluent about 45° thus promoting its vaporization but chiefly to reduce any tendency toward the deposition of any gummy solids in the transfer line 14. This flux liquid is drawn off near the bottom of the separator 18 in pipe 16 and recirculated by pump 22 at the rate of 9,220 lbs./hr. or 720 b./d.

This liquid is composed of the higher boiling hydrocarbons of the initial reactor effluent which are retained in the liquid phase and a small quantity of dissolved polymeric material. The latter is a by-product of the present process and is readily soluble in the benzene and other aromatic hydrocarbons constituting most of the liquid flux.

Two other modes of heating the first reaction effluent are also employed during its passage to the vaporizer pot 18. Saturated steam at 220 p.s.i.g. is admitted to the heater 15 under a control technique described hereinafter to indirectly heat the first reaction products to a temperature of 337°. In addition, a heated hydrogen-rich gaseous mixture is injected into those initial products in conduit 20 upstream but close to the chamber 18. This hydrogen-rich stream is part of that drawn off in line 8 from the total circulating gas (recycle and make-up gases) in conduit 6. The gas in pipe 8 flows through the heat exchanger 24 where its temperature is raised to 380° and finally into gas-fired heater 26. Firing of this heater is controlled in a unique manner which is described later; and it provides an effluent leaving in conduit 28 at a temperature of 645°, which is divided by means of the three-way valve 30 with 20% of the total circulating gas being introduced into pipe 32 and the remaining 30% passing through conduit 34 to join the first reaction effluent in line 20. This further heating of the product stream in line 20 of course results in more vaporization and vaporization is completed to the desired extent in the flash chamber and separator 18. The latter is a vessel of enlarged cross section with an internal diameter of 4.5 feet and a height of 12.5 feet which provides favorable conditions for the substantially complete separation of the gaseous phase from the liquid phase in a mixture thereof at a temperature of 360° and pressure of 695 p.s.i.g.

Based on the rate of feeding pyrolysis gasoline, 4% of said liquid feed and reaction products thereof vaporizes in reactor 12, about 75% more is evaporated during passage through line 14 and heater 15, further vaporization is produced by the hot gas injected from pipe 34 and only 8.5% is collected in the liquid phase in the vaporizer pot 18 in addition to the circulating flux.

The gaseous phase going overhead passes through the demister blanket or pad 36 of coarse steel wool designed to catch any entrained droplets of liquid. No substantial deposition of polymers or gums occurs in the lines 14 and 20 or heater 15, but the liquid in the bottom of pot 18 contains an amount of dissolved polymer (ASTM gum content=67 mg./100 ml.) which is small but sufficient to foul and thereby deactivate a contact catalyst within a fairly short time, particularly at desulfurizing temperatures, of 450° and higher. A portion of the flux is continually being removed at a constant rate of 200 b./d. as spent flux through the bottom line 38 under the regulation of the flow controller 40 operating the automatic valve 42. The rate of withdrawing spent flux from the system is manually reset on that controller from time to time to the minimum rate that will hold the gum content thereof below about 100 milligrams per 100 mls. The spent liquid flux is transferred to a rerun tower (not shown).

While an extraneous flux may be alternatively supplied to the system at a constant rate through the line 50 connected to separator 18, a suitable flux is obtained from the effluent of the first reactor by temporarily operating heater 15 in the manner described hereinbefore to accumulate sufficient liquid in pot 18 for recycling as a flux; and thereafter normal operating conditions are employed in the vaporizing system. The overhead or vapor phase passes through heat exchanger 52 on its way from separator 18 via conduit 54 to join the hydrogen-rich gas from pipe 32 in line 56 as the charge for the second reactor 58. In this passage, the heat exchanger 52 raises the temperature of the overhead effluent to 485° and ad-

mixture with the hydrogen-rich gas at about 645° further raises the temperature of the total charge to 515° at the reactor inlet.

As indicated previously, two temperature control techniques are employed for heating and thereby vaporizing liquid effluent from the first reactor to prepare a vapor phase charge for the second reactor. First, the rate of flow of heating steam through conduit 59 to heater 15 is controlled by automatic valve 60 in response to an external liquid level controller 62 which is connected in conventional manner to sense the liquid level in separator pot 18. Since the rates of circulation of flux liquid and removal of the spent flux are customarily held constant, a rise in the level of liquid in pot 18 indicates that the liquid feed stock and its liquid products are being vaporized at a lower rate. This is corrected automatically by the level controller 62 generating a function or signal in response to which valve 60 automatically opens to admit more steam into heater 15 and thus vaporize more of the first reactor effluent passing through the heater 15. Conversely, a fall in liquid level in the vaporizing chamber indicates that a greater proportion is being vaporized, and this is corrected by a signal from the level controller 62 to the automatic valve 60 which reduces the steam input to heater 15, and therefore results in a lower rate of vaporization in the liquid passing therethrough.

The firing of the furnace 26 for heating hydrogen-rich circulating gas is controlled by the automatic valve 64 operating in the fuel gas supply line 66 in response to two temperature controllers. Temperature controller 68 senses the temperature in the outlet line 28 from the heater and maintains a temperature 645° at this point, but this device is reset to other temperatures as may be required in response to the temperature controller 70 which is connected to conduit 56 and maintains a temperature of 515° in the charge entering the second reactor.

Reactor 58 contains two beds of contact catalysts. Upper bed 71 made up of 1% platinum on chi alumina of $\frac{3}{16}$ " particle size occupies 10% of the catalyst space in the second reactor and the other 90% is filled with the lower bed 72 of desulfurization catalyst. A horizontal perforate plate or screen (not shown) with openings of $\frac{1}{8}$ " maximum dimension is located at the boundary between the upper intermediate hydrogenation zone and the lower desulfurization zone. This plate supports the upper

size prepared by hydrogen sulfide treatment in the manner described hereinbefore with a sulfur content of 4.6% at operating equilibrium and a weight ratio of $\text{Al}_2\text{O}_3:\text{Mo}:\text{Co}$ of 84.7:7.9:2.7 respectively.

The less reactive diolefins remaining in the initial reaction effluent are saturated in the second reactor along with all of the mono olefins that remain in a nondestructive manner and with no substantial saturation of aromatic compounds. Most of this addition of hydrogen to unsaturated compounds occurs in the intermediate hydrogenation (upper) zone. The reaction conditions in the second reactor are as follows:

Inlet temperature	degrees	515
Average reaction temperature:		
Upper zone 71	do	535
Lower zone 72	do	555
Outlet temperature	do	555
Total pressure	p.s.i.g.	685
H_2 partial pressure (inlet)	p.s.i.	345
Total H_2 charged	s.c.f./b	3950
Space velocity-LHSV:		
Upper zone 71		17
Lower zone 72		1.9
Upper zone catalyst activity indexes:		
Hydrogenation		100
Polymerization		<22
Desulfurization		0
Lower zone catalyst activity indexes:		
Desulfurization		98-100
Polymerization		43

From the inlet and outlet temperatures given, it is apparent that significant hydrogenation reactions with substantial exotherms are taking place in both reactors. This is borne out by a comparison of the unsaturation indexes of column 4 with column 5 in Table I hereinafter and also of column 6 with 7. The latter two indicate that a minor hydrogenation of diolefins is completed in the final reactor along with the principal hydrogen treatment that saturates substantially all of the remaining half of the mono-olefins and a substantially complete hydrodesulfurization of organic sulfur compounds. Again there is no appreciable polymerization or deposition of coke and no noticeable conversion of aromatic hydrocarbons to naphthenes occurs.

Table I

Stream	1 Gasol. Feed	2 Fresh H_2 -Rich Gas	3 Total H_2 -Rich Gas	4 First Reactor Charge	5 First Reactor Effluent	6 Final Reactor Charge	7 Final Reactor Effluent	8 H.P. Sep. Off Gas	9 Stabilizer Off Gas	10 Stabilized Liquid
Flow, lbs./hour	28,220	2,520	14,020	35,230	35,230	39,680	39,680	1,860	920	25,400
Gravity, °API	36.8									37.5
Ave. Mol. Wt.	79.8	8.4	9.0	31.1	31.2	22.9	22.9	9.1	28.0	80.1
Bromine No.	24			24	12	12	Nil			Nil
Diene No.	13.5			13.5	1.5	1.5	Nil			Nil
Percent Vaporized ¹	Nil			Nil		91.5				
Organic S, p.p.m. ¹	450			450	450	450	10			10
Mols per Hour:										
H_2		195.0	961.0	480.5						
C_1		79.5	501.2	250.6						
C_2		20.1	68.3	34.2						
H_2S (in p.p.m.)		(10)								
C_3		4.2	10.1	5.1						
C_4		0.9	1.3	0.7						
C_5 Saturates	0.9	1.8	2.3	1.2						
C_5 Unsaturates	3.4			3.5						
C_6 Saturates	29.7		3.1	31.9						
C_6 Unsaturates	29.7			30.6						
Benzene	270.4		13.6	277.2						
Toluene	3.5		0.1	3.6						
Other C_7+	16.1			15.3						
Total, Mols/Hr.	353.7	300.0	1,560.9	1,134.2						

¹ Based on weight of original liquid feed.

bed and prevents any appreciable intermingling of the two catalysts.

The lower bed is a composite of cobalt and molybdenum sulfides on a gamma alumina of $\frac{3}{16}$ inch particle

The gaseous product stream leaves the bottom of reactor 58 via conduit 74 and is cooled by passing through heat exchangers 52 and 24 respectively, as well as the cooler 76, on its way to the second separator 78 where the vapor

phase is separated from the newly condensed liquid at a temperature of 100° and pressure of 640 p.s.i.g. From this vessel the gaseous phase is taken overhead in lines 80 and 82. About 15% of this gas is bled off to the refinery fuel system through pipe 84 and the pressure regulator 86 which maintains the desired pressure on the hydrogenation system. The rate of removal of this separator gas from the instant system is tabulated in column 8 of Table I. Most of the gaseous material, however, enters the line 90 wherein it meets with any make-up gas that also may require scrubbing to remove excessive hydrogen sulfide which make-up gas is drawn from supply conduit 4 via valved line 92. These gases are introduced into the lower half of the combination washer 94 which is equipped with a lower caustic scrubber section 96 beneath a water washing section 98.

Fresh aqueous sodium hydroxide solution is admitted in conduit 100 and joins recirculating caustic soda solution in the line 102 on its way to the perforated scrubber trays over which it cascades downwardly against the rising gases. This alkaline liquid is drawn off through the conduit 106 at the bottom and divided between an exit line 108 for spent solution and conduit 110 leading to the recirculation pump 112.

Cold water is admitted to the section 98 of the tower from supply line 114 and is drawn off through the valved conduit 116. It will be noted that substantially all of the water is collected in the trough 118 and is not allowed to descend therebelow and dilute the caustic scrubbing solution. The gases rising countercurrently through the tower 94 at 640 p.s.i.g. lose most of their hydrogen sulfide content in being scrubbed first by intimate contact with curtains of caustic soda solution, next they pass through the demisting pad 120 into the washing section where they are washed with curtains of falling water to remove the last traces of H₂S as well as any entrained particles of the caustic soda solution and then through the demisting pad 122.

The scrubbed and washed gases exit through the conduit 124 which connects with the valved by-pass line 126, that may be used to divert some or all of the separator off-gas around tower 94. The by-pass conduit is useful when the hydrogen sulfide content of the separator gas is low enough for a recycle gas. These two pipes feed into the line 128 which leads to the knockout pot 130 in which any entrained liquid is separated. From here the hydrogen-rich gas passes through conduit 132 to compressor 134 where its pressure is boosted sufficiently to circulate it through the recycle gas line 6 and associated conduits in the manner described earlier.

Returning now to the scrubber 94, it is apparent that an extremely flexible arrangement is shown for controlling the hydrogen sulfide content of the circulating gases passed into the two reactors with the feed. For example, the operator can divide the gaseous product from separator 78 between inlet line 90 of the caustic scrubber and the by-pass conduit 126 in any desired proportions. Similarly, the make-up gas entering in conduit 4 can be introduced directly into circulating gas line 6 or part or all of it can be taken off via conduit 92 for treatment in the caustic scrubber. Also, either or both of the rates of recirculation or caustic soda solutions in scrubber section 96 and the introduction of fresh caustic soda thereto can be controlled to set the rate of reaction and removal of hydrogen sulfide from the gas stream passing through the tower.

The liquid phase withdrawn from the bottom of high pressure separator 78 is treated in the stabilizing tower 136 at 180 p.s.i.g. after being carried in the conduit 138 through the pressure reducing valve 140 and heat exchanger 142 in which the temperature of the stream is raised to 240° F. Attached to the 30-tray stabilizer are valved inlet lines 144 to 146 to introduce the charge selectively and in any proportions onto the 18th and 12th trays respectively counting from the bottom of the col-

umn. A reboiler 148 is provided to maintain the bottoms at a temperature of about 385° F. and a stable, substantially saturated liquid product is withdrawn as the product of the process via pipe 150 into heat exchanger 142 at the rate given in column 10 of the table. This liquid, rich in aromatic hydrocarbons, is suitable for extraction processes, such as extraction with diethylene glycol, for the concentration of aromatics by reason of its negligible content of diolefins, olefins and sulfur. It is essentially a mixture of paraffinic and aromatic hydrocarbons, and a sharp separation can readily be obtained between these constituents.

An overhead fraction is conveyed via the conduit 152 and cooler 154 in which cold water reduces its temperature from 295 to 125° in transit to the reflux accumulator 156. Liquid reflux is returned from the bottom of this accumulator to the stabilizer 136 through line 158 and pump 160 at a rate of 9840 lbs. per hour and a gaseous by-product of the process is withdrawn through the valved conduit 162 at the rate set forth in column 9 of Table I for use as fuel or other suitable purposes.

Starting up the process described herein in a commercial plant is relatively free of difficulties. Make-up gas obtained from a catalytic reformer is charged at ambient temperature and the usual operating partial pressure of hydrogen into the initial reactor 12 and also through the furnace 26 into the final reactor 58. This is continued until the heat carried by the gas from the furnace brings the second reactor close to its normal operating temperatures. Meanwhile, recycle gas is substituted for most of the fresh supply of hydrogen rich gas after a thorough purging of the system. Next a typical reformate derived from naphtha and relatively free from unsaturated aliphatic compounds is introduced as a temporary feed along with the circulating gas. An unusually high proportion of liquid accumulates in the separating chamber 18 from the time the reformate is first charged until that chamber reaches normal operating temperature and none is withdrawn through the spent flux line at first. After the circulating flux system is allowed to fill up with the liquid phase collecting in the vaporizer chamber, liquid is drained off in the spent flux line at an abnormally high rate until normal feed is being processed at normal vaporizing temperatures. The final step is to gradually blend the regular pyrolysis liquid feed stock into the reformate in gradually increasing proportions with a corresponding reduction in the supply of the reformed product until the latter component is shut off completely.

EXAMPLE 2

Several considerably broader cuts of pyrolysis gasoline are subjected to a multistage hydrogen treatment with a different combination of catalysts. A platinum catalyst is charged into the initial reactor of a pilot plant. The upflow second reactor contains a bottom bed (9% of the total catalyst volume of the second reactor) of the same platinum catalyst used in the first reactor, and the upper bed consists of 91 volume percent of 15.3% by weight of unsulfided cobalt molybdate on gamma alumina. The gas charged is hydrogen of commercial purity in place of the usual refinery and recycle gases containing substantial contents of lower hydrocarbons such as methane. In these small scale operations, it is not feasible to recirculate the flux or even remove the spent flux continuously; but highly colored spent flux with a significant gum content is withdrawn from the bottom of a separator located between the two reactors at intervals of 8 hours in quantities equal to 0.5% by weight of the pyrolysis liquid charged. The liquid phase of the initial reactor effluent is vaporized by injecting hot hydrogen into the aforesaid separator and also by controlled electrical heating elements wrapped around the separator.

Other reaction conditions and the results obtainable during a lengthy operation are set forth in Table II. No fouling from excessive formation of coke or polymers

is encountered and it is apparent that the process described is not only of an extremely flexible nature but is also capable of operating for extremely long periods without halting for regeneration.

the examples without departing from the invention. For instance, standby units arranged in parallel with alternate piping may be provided for all equipment that requires periodic regeneration or cleaning. Accordingly, the pres-

Table II

	1st Reactor						2nd Reactor					
Reaction Conditions:							9 vol. percent (1% Pt/alumina) 91 vol. percent (Co-Mo/alumina)					
Catalyst	450	450	450	450	450	450	450	450	450	450	450	450
Total Pressure, p.s.i.g.	400	400	400	400	400	400	330	330	330	330	330	330
Inlet H ₂ , p.s.i.	1,500	1,500	1,500	1,500	1,500	1,500	2,000 additional	20 in Pt Cat	2.0 in Co-Mo Cat.	500	500	500
H ₂ Charge, s.c.f./h	2.0	2.0	2.0	2.0	2.0	2.0	500	500	500	500	500	500
Space Velocity, LHSV	225	225	225	225	225	225	520	516	528	540	515	559
Av. Reactor Temp., ° F	5.3	11.1	18.0	26.1	32.7	107	5.0	10.8	18.0	26.7	33.7	100
Av. Temp., 2nd Pt Cat												
Cat. Age, Days												
Charge Stock:												
Bromine Number	39.9	39.9	43.7	43.7	25.4	25.8						
Diene Number	29	29	29	29	16	18						
Sulfur, p.p.m.	170	170	190	190	185	200						
Initial B.P., ° F	120	120			142	161						
End Point, ° F	314	314			280	266						
Product:												
Bromine Number	17.2	18.3	25.3	27.4	16.0	22.7	0.1	0.3	0.3	0.9	0.2	0.3
Diene Number	Nil	1	4	6	3	13					Nil	
Sulfur, p.p.m.		160			160		5	9			5	9
Catalyst Performance:												
Percent Reduction, Br. No.	57	54	42	37	37	12						
Percent Reduction, Diene No.	100	97	87	79	81	28						

¹ Average Reaction Temperature of only the cobalt molybdate catalyst bed.

EXAMPLE 3

A different combination of catalysts is employed in the equipment used in Example 2 in hydrogenating another batch of pyrolysis gasoline to further illustrate the present invention. The intermediate hydrogenation zone in the upper 20% of the catalyst space is filled with a catalyst comprising 1% palladium on gamma alumina in the form of $\frac{3}{16}$ " extruded pellets. The balance of the catalyst volume contains $\frac{3}{16}$ " gamma alumina bearing 3% cobalt oxide and 12% molybdenum oxide.

Significant reaction conditions and results are tabulated in Table III.

Table III

Reaction Conditions	1st Reactor	2nd Reactor
Catalyst	(¹)	(²)
Total Pressure, p.s.i.g.	500	500
H ₂ Partial Pressure, p.s.i.	450	350
H ₂ Charge, s.c.f./h	3,000	3,500
Space Velocity, LHSV	2	3.2
Av. Reactor Temp., ° F	230	260
Av. Temp. of Pd. Cat., ° F		530
Catalyst Age, Days	7.1	7.1
Product	Charge	
Bromine No.	70	46
Diene No.	45	1
Sulfur, p.p.m.	640	380
I.B.P., ° F	140	
E.P., ° F	260	

¹ 55% Ni on kieselguhr.

² 20 vol. percent Pd/alumina, 80 vol. percent Co-Mo/alumina.

³ Co-Mo.

The selectivity of the nickel catalyst for hydrogenating dienes in preference to mono-olefins is apparent upon comparing the Diene No. of 1 and Bromine No. of 46 for the first stage product with the values of 8 and 40 respectively that are obtained with the same feed and reaction conditions except for substituting the 1% platinum catalyst of Example II.

The detailed examples given hereinbefore are intended only to illustrate the invention. It will be apparent to those skilled in the art that many other modifications and variations may be made in the embodiments set forth in

ent invention is not to be considered as limited in any respect other than the recitals of the appended claims.

Certain aspects of the reactions and/or the vaporization between reaction stages which are disclosed hereinbefore are described also and claimed in application Ser. No. 238,693 filed November 19, 1962 of Raymond R. Halik et al. entitled "Selective Hydrogenation of Hydrocarbons" and application Ser. No. 238,690 filed November 19, 1962 of Richard G. Graven et al. entitled "Selective Conversion of Unstable Liquids."

What is claimed is:

1. A process for the selective nondestructive hydrogenation of a liquid hydrocarbon feed boiling below about 500° F. and containing aromatic hydrocarbons, olefins, diolefins and sulfur compounds which comprises passing said feed in the liquid phase and hydrogen through an initial hydrogenation zone in contact with a porous solid hydrogenation catalyst having a high hydrogenation activity and a low polymerization activity while controlling hydrogenating conditions in said zone to provide a hydrogenation effluent from said zone in which a substantial amount of the diolefins have been at least partially saturated and in which a substantial part of said liquid feed and products thereof are in the liquid phase, vaporizing liquid in said initial hydrogenation effluent, passing the resulting vapors together with hydrogen through an intermediate hydrogenation zone in contact with a porous solid hydrogenation catalyst having a high hydrogenation activity and a low polymerization activity at a temperature substantially higher than the average temperature in said initial zone under conditions controlled to further hydrogenate said vapors, passing the effluent from said intermediate zone through a subsequent conversion zone at a suitable desulfurization temperature in contact with a porous solid sulfur-resistant conversion catalyst having at least moderate hydrogenation activity and a high desulfurization activity, and regulating conditions in said conversion zone to produce a substantially desulfurized conversion effluent with a normally liquid fraction having a substantial lower Bromine Number than said liquid feed.

2. A process for the selective nondestructive hydrogenation of a liquid hydrocarbon feed boiling below

about 500° F. and containing aromatic hydrocarbons, olefins, diolefins and sulfur compounds which comprises passing said feed in the liquid phase and hydrogen through an initial hydrogenation zone in contact with a porous solid hydrogenation catalyst having a high hydrogenation activity and a low polymerization activity while controlling hydrogenating conditions in said zone to provide a hydrogenation effluent from said zone in which at least about 35% of the diolefins have been at least partially saturated and in which a substantial part of said liquid feed and products thereof are in the liquid phase, vaporizing liquid in said initial hydrogenation effluent, passing the resulting vapors together with hydrogen through an intermediate hydrogenation zone in contact with a porous solid hydrogenation catalyst having a high hydrogenation activity and a low polymerization activity at a temperature high enough for olefin saturation and substantially higher than the average temperature in said initial zone under conditions controlled to further hydrogenate said vapors whereby the diolefin content of the normally liquid fraction thereof is less than about 50% of that of said liquid feed, withdrawing the effluent from said intermediate zone at a temperature suitable for desulfurization, passing said intermediate effluent through a subsequent conversion zone in contact with a porous solid sulfur-resistant conversion catalyst having at least moderate hydrogenation activity and a high desulfurization activity, and controlling conversion conditions in said conversion zone to produce an effluent with a normally liquid fraction having a Bromine Number less than about 4 and an organic sulfur content below about 20 p.p.m.

3. A process according to claim 2 in which the temperature in said intermediate zone is also high enough for desulfurization.

4. A process according to claim 2 in which at least about 50% of the more reactive diolefins are at least partially saturated in said initial zone and the diolefin content of the normally liquid fraction of said intermediate effluent is less than about 40% of that of said liquid feed.

5. A process according to claim 2 in which the charge to said intermediate zone contains a sulfur compound in the gaseous phase having a hydrogenation-inhibiting effect equivalent to 50 p.p.m. of thiophene sulfur and the partial pressure of hydrogen sulfide in said zone is maintained below about 0.05 p.s.i.a., whereby conversion of aromatic hydrocarbons into naphthenes is substantially prevented without substantially deactivating said intermediate hydrogenation catalyst.

6. A method according to claim 2 in which said initial and intermediate catalysts have hydrogenation activity indexes of at least about 40, sulfur-free benzene conversion indexes above about 50 and polymerization activity indexes less than about 35; and said conversion catalyst has a sulfur-free benzene conversion index below about 25, a fresh desulfurization activity index of at least about 80 and a polymerization activity index above about 25.

7. A method according to claim 2 in which said initial and intermediate catalysts each contain a metal of Group VIII of the Periodic Table of Elements having an atomic number of at least 27, and said conversion catalyst contains a metal of the iron group and a metal in Group VI B of said Periodic Table.

8. A method according to claim 2 in which said initial and intermediate catalysts comprise platinum supported on the surface of particle form alumina and said conversion catalyst comprises sulfides of cobalt and molybdenum supported on the surface of particle form alumina.

9. A method according to claim 2 in which said initial catalyst comprises palladium supported on the surface of particle form alumina, said intermediate catalyst comprises platinum supported on the surface of particle form alumina said said conversion catalyst comprises sulfides of cobalt and molybdenum supported on the surface of particle form alumina.

10. A method according to claim 2 in which said initial catalyst comprises between about 0.05 and 10.0% palladium supported on the surface of particle form alumina, said intermediate catalyst comprises between about 0.05 and 2.0% platinum supported on the surface of particle form alumina and said conversion catalyst comprises compounds of cobalt and molybdenum supported on the surface of particle form alumina.

11. A method according to claim 2 in which the temperature of said intermediate effluent is not substantially changed between said intermediate zone and said conversion zone.

12. A method according to claim 2 in which said intermediate zone and said conversion zone are located in a single closed reaction vessel.

13. A method according to claim 2 in which said intermediate catalyst and said conversion catalyst are employed in volumetric ratios between 1:40 and 1:2, respectively.

14. A method according to claim 2 in which the conditions controlled within said initial zone include maintaining a hydrogen partial pressure within the range of about 200–800 p.s.i., an hourly space velocity within the range of about 0.2–15.0 based on the volume of said liquid feed, a hydrogen charge within the range of about 500–5000 s.c.f./b. of said liquid feed and a feed temperature within the broad range of about 75–300° F., the conditions controlled in said intermediate zone include maintaining a hydrogen partial pressure within the range of about 200–800 p.s.i., an hourly space velocity within the range of about 2–60 based on the volume of said liquid feed, a total hydrogen charge within the range of about 500–10,000 s.c.f./b. of said liquid feed and an inlet temperature within the wide range of about 350–700° F.; and the conditions controlled in said conversion zone include maintaining an hourly space velocity between about 0.2 and 8 based on the volume of said liquid feed and an average reaction temperature not substantially below said inlet temperature of the intermediate zone.

15. A method according to claim 14 in which said feed temperature is maintained within the narrow range of 75–190° F. while said catalyst is fresh and said temperature is increased within the limits of said broad range to maintain said diolefin saturation as the hydrogenation activity of said initial catalyst decreases with continued use, and said inlet temperature to the intermediate zone is maintained within a narrow range of about 400–550° F. while said intermediate and conversion catalysts are fresh and said inlet temperature is increased within said wide range as the activity of said catalysts decreases with continued use in order to maintain said organic sulfur content and Bromine Number in said conversion effluent fraction.

16. A method according to claim 2 in which the conditions controlled within said initial zone include maintaining a hydrogen partial pressure within the range of about 300–600 p.s.i., an hourly space velocity within the range of about 0.5–8.0 based on the volume of said liquid feed, a hydrogen charge within the range of about 1200–3000 s.c.f./b. of said liquid feed and a feed temperature within the range of about 75–250° F. to provide a hydrogenation effluent from said zone in which the Bromine Number of the normally liquid fraction thereof is at least 25% below that of the liquid feed and at least about 50% of the diolefins have been at least partially saturated and in which an amount equal to at least about 60% of the liquid feed is in the liquid phase; the conditions controlled in said intermediate zone include maintaining a hydrogen partial pressure within the range of about 300–600 p.s.i., an hourly space velocity within the range of about 5–40 based on the volume of said liquid feed, a total hydrogen charge within the range of about 2000–5000 s.c.f./b. of said liquid feed and an inlet temperature within the range of about 400–650° F. to provide an intermediate

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zone effluent with a normally liquid fraction in which the diolefin content is less than about 40% of that of said liquid feed; and the conditions controlled in said conversion zone include maintaining an hourly space velocity between about 0.5-5 based on the volume of said liquid feed and an average reaction temperature not substantially below said inlet temperature of the intermediate zone to produce an effluent with a normally liquid fraction having a Bromine Number less than about 2.0 and an organic sulfur content below about 15 p.p.m.

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DELBERT E. GANTZ, *Primary Examiner.*10 ALPHONSO D. SULLIVAN, *Examiner.*