

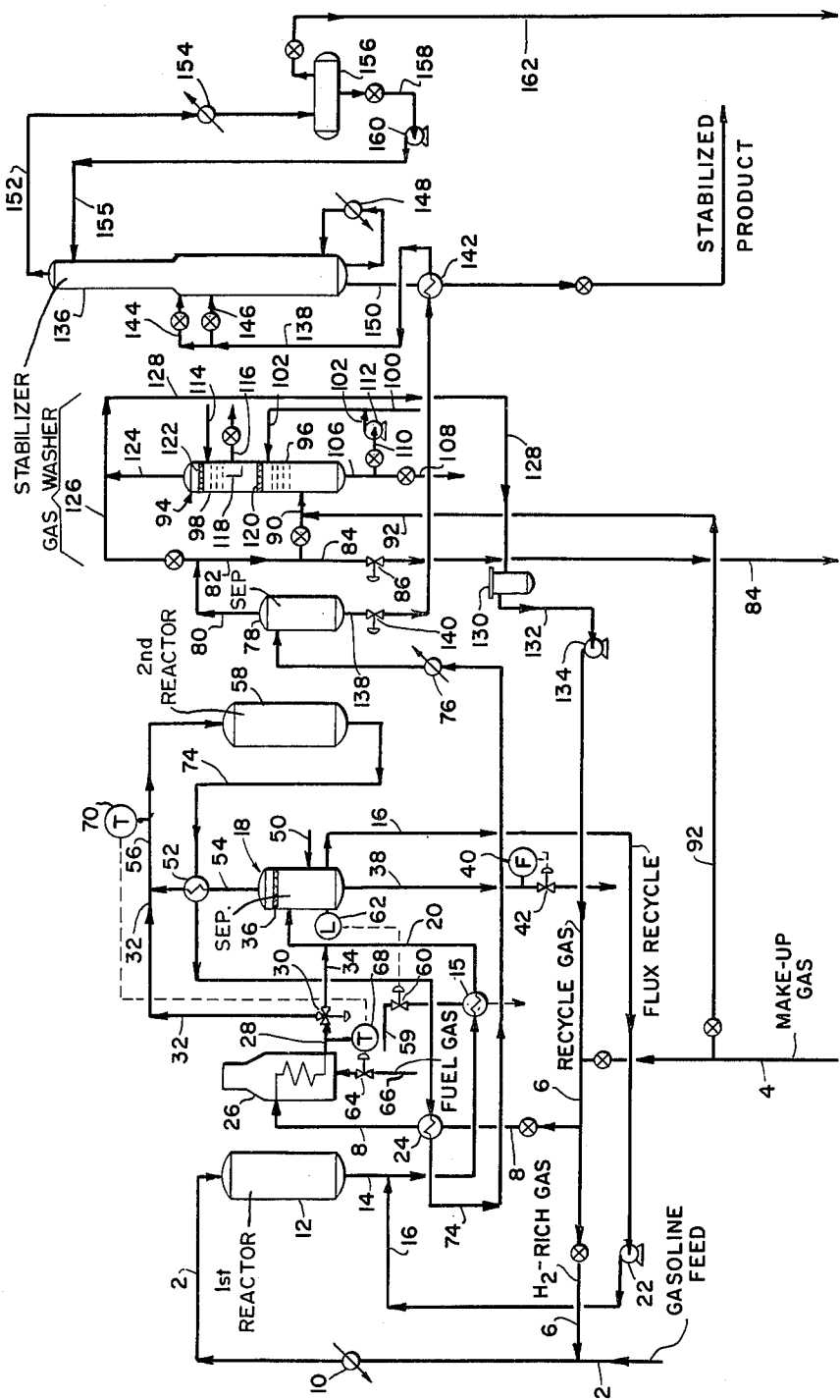
March 8, 1966

R. R. HALIK ETAL

3,239,453

SELECTIVE HYDROGENATION OF HYDROCARBONS

Filed Nov. 19, 1962



1

3,239,453

## SELECTIVE HYDROGENATION OF HYDROCARBONS

Raymond R. Halik, Pitman, Fritz A. Smith, Cherry Hill, and Carl W. Streed, Sewell, N.J., and Richard G. Graven, North Castle, N.Y., assignors to Socony Mobil Oil Company, Inc., a corporation of New York  
Filed Nov. 19, 1962, Ser. No. 238,693  
26 Claims. (Cl. 208—210)

The present invention relates to a process, preferably of the continuous type, for the selective hydrogenation in 2 or more 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 re-forming 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 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, 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 or 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.

2

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.

Another object of the invention is to provide a process for hydrogenating a mixture boiling below 500° F. of aromatic and unsaturated aliphatic hydrocarbons without the formation of significant quantities of naphthenes or polymers.

A further object of the invention is to provide an improved process for the selective, nondestructive hydrogenation of unstable products with a boiling range below about 500° F. derived from thermally cracking petroleum fractions, which hydrogenation is performed in stages of increasing severity without excessive deactivation of the contact catalysts.

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 still further object of the invention is to provide an improved process for the selective hydrogenation of an unstable hydrocarbon mixture in which only a small amount of polymeric material is formed and is thereafter removed from the intermediate product stream prior to the final hydrogenation reaction.

Yet another object of the invention is to provide an improved process for the selective hydrogenation of an unstable hydrocarbon mixture wherein a single liquid medium is utilized to supply heat for vaporizing at least some of the liquid in an intermediate product stream for a subsequent vapor phase reaction and also to remove polymeric material from contact with said intermediate product stream.

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 a 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 within certain specified ranges to provide a hydrogenation effluent in which at least about 35%, and preferably at least about 60%, of the diolefins have been at least partially saturated and in which an amount equal to at least 20%, and preferably at least 60%, of the liquid feed remains in the liquid phase. In a preferred modification, the Bromine Number of the normally liquid fraction of said effluent is also reduced at least 25% below that of the liquid feed. Said conditions which are regulated there include maintaining a hydrogen partial pressure within the range of about 200–800 (about 300–600 being preferred) pounds per square inch absolute pressure (hereinafter abbreviated p.s.i.a.), an hourly space

velocity within the range of about 0.2–15.0, and preferably about 0.5–8.0, based on the volume of liquid feed, the hydrogen charge within the range of about 500–5000, and preferably about 1200–3000, standard cubic feet per barrel (hereinafter abbreviated s.c.f./b.) of liquid and a feed temperature within the broad range of about 75–300° F., and preferably not over about 250°. Controlled vaporization of liquid in said hydrogenation effluent and separation of the gaseous phase thereof is effected in the presence of a liquid flux, for example an amount of flux equal to at least about 5%, and preferably over 10%, of said liquid feed. This flux may be any liquid substance or mixture which is miscible with and unreactive with said liquid feed including immediate reaction products, recycled partially or fully hydrogenated products of the instant process or extraneous liquids, preferably 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. Hydrogen together with gaseous material derived from said vaporization step are passed through a subsequent conversion zone in contact with a porous solid conversion catalyst of at least moderate hydrogenation activity and high desulfurization activity at a substantially higher average temperature than in said initial zone while regulating conversion conditions within certain specified ranges to produce a conversion effluent with a normally liquid fraction having a Bromine Number less than about 4, preferably below about 2, and an organic sulfur content below about 20 p.p.m., and preferably below 15 p.p.m. The specified ranges of conversion conditions include maintaining a hydrogen partial pressure within the range of about 200–800 (about 300–600 being preferred) p.s.i.a., an hourly space velocity within the range of about 0.2–6.0 (about 0.5–4.0 being preferred) based on the volume of original liquid feed, the total hydrogen charge (unreacted hydrogen plus any newly introduced hydrogen) within the range of about 500–10,000 (preferably about 2000–5000) s.c.f./b. of said liquid feed and an inlet temperature within the wide range of about 350–700°, and preferably about 400–650° F.

Narrower aspects of the invention include feeds of narrower boiling ranges, designated ranges of catalyst activities, increasing said feed and inlet temperatures as catalyst activity decreases, recirculating the flux, removing polymeric byproducts between reaction stages, the extent and the regulation of said controlled vaporization step and said preferred reaction conditions.

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 finally treated in the gaseous phase with hydrogen under more severe conditions. The initial hydrogenation is conducted at a temperature sufficiently low to avoid or minimize both thermal and catalytic polymerization while hydrogenating a substantial portion and usually all or almost all of the diolefins, including all of the more reactive ones. During the initial hydrogenation, little, if any, desulfurization is accomplished and a substantial proportion of the mono-olefins usually remain 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 and 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 desulfurization and also for olefin saturation and then it is subjected to a catalytic conversion with hydrogen at a distinctly higher temperature than in the initial hydrogenation. In this 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 catalyst is customarily of a type of high polymerization potential.

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 final reactor that the exotherm there is quite small with little temperature difference being noted between the inlet and outlet. Eventually as the activity of the catalyst in the first reactor decreases with continued use, more of the hydrogenation load is shifted to the second or final reactor and substantial increases between the inlet and outlet temperatures of this reactor are then apparent.

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°.

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 22 which measure the proportions 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 as high as about 40 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 700 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% aromatics 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 in 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 within 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 150–800 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 and the consumption is usually found to be less than 500 s.c.f./b. Substantial excess of hydrogen have been specified hereinbefore to avoid a drop in the hydrogenation rates as a result of an inadequate supply of hydrogen. Although pure hydrogen may be used, it is customarily supplied as a mixture of hydrogen and gaseous hydrocarbons in the off gases of units for reforming naphthas or hydrosulfurizing 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.

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.a., in which the 300–600 p.s.i.a. range is 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. 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 the theory of 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 co-incident deposition of polymeric gum or coke. Such deposition can occur at temperatures of 300° and 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 desirably 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 remainder may be introduced into the wholly gaseous stream leaving the top of said chamber on its way to the second stage conversion 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 its polymerization activity must be relatively low in order to avoid the formation of gums which will deactivate the catalyst. While suitable hydrogenation catalysts also incidentally possess relatively high desulfurization activity initially, this property 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 quantities 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 catalyst, 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 such catalysts under the specified reaction conditions. A suitable catalyst for the initial reactor 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 with the preferred catalysts.

Another means for designating suitable catalysts for the first reactor 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 first reactor 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 desulfurization 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 must have 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 good catalysts for the initial hydrogenation zone also have desulfurization indexes in the 80–100 range initially but these 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 not desirable for 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.

A variety of catalysts of differing chemical constitution may be employed in the initial hydrogenation step 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, 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. Nickel, either unsupported or on known 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. 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. Among the many suitable specific catalysts are 5% palladium on activated carbon and 0.6% platinum on eta 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 catalyst or catalysts employed in the second or a final reactor operate under quite different reaction conditions from those in the initial reactor. The charge is entirely in the gaseous phase and substantially higher temperatures are required in the second reactor to desulfurize the intermediate product and to complete the hydrogenation of the less reactive unsaturated hydrocarbons, namely the mono-olefins and any remaining diolefins. This catalyst may also be defined in terms of an arbitrary desulfurization activity index activity as set forth hereinbefore in the 80–100 range, which is retained for a period of at least one week and usually much longer. It should 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 stage 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 hydrogenation of the more reactive diolefins in the charge to the final desulfurization stage, there is little tendency for polymerization to occur. The preferred catalyst for the final stage is a sulfided composite of cobalt molybdate on the surface of gamma alumina.

In illustration, the presulfiding or final step in the preparation of a preferred type of desulfurization catalyst may desirably be performed in situ in the reactor. 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 prereduction 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.a. for hydrogen sulfide and 100 p.s.i.a. in the case of hydrogen while 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 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, 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 at least about 35%, and preferably at least 60%, of the original diolefins have been converted into mono-olefins or paraffins and in which an amount equal to at least about 20%, and preferably at least about 60%, of the liquid feed rate remains in the liquid phase. It is also preferred to obtain an effluent liquid fraction with 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, 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 a 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. The feed temperature should of course be within the stated range and, in the preferred operation, the feed temperature is maintained at a substantially constant value within the narrow range of 75–190° F., and desirably in the lower part of that range, while the catalyst is fresh. Generally, this temperature is subsequently increased either gradually or by steps but not beyond about 300° F. in order to maintain a diolefin saturation above the specified minimum, and preferably 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 required when the Diene Number reduction is less than the prescribed minimum of 35%, or the degree of vaporization exceeds 80%, or both, even after the feed temperature has been adjusted upward to the stated maximum. 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 temperature ranging up to end points near 500°.

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 necessary proportion of liquid phase effluent 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 define 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 stated reaction conditions can reach a temperature sufficiently high to deactivate the catalyst. 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 their activity for extremely long periods, as for instance, 3 months or more in the case of palladium catalysts, regeneration of the catalyst is eventually necessary and 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 or 2% oxygen therethrough. 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 the purpose and the more convenient medium of steam may be utilized as the diluent with a palladium catalyst.

The desulfurization or final stage catalyst is conventionally regenerated in similar fashion at even longer intervals of about 6 months or more. In the case of a sulfided composite of cobalt and molybdenum on alumina, this converts the cobalt and molybdenum compounds to oxides and a presulfiding treatment such as the one described hereinbefore is employed to restore the catalyst to its original form.

It has also been found that purging the initial catalyst with hydrogen at 200–500 p.s.i.a. and 750–850° for 16–48 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, this catalyst may be regenerated several times by such treatment with hydrogen-rich gas before it is necessary to regenerate the contact agent by the combustion technique.

Only a limited amount of hydrogen sulfide may be tolerated by certain of the catalysts suitable for the first stage reactor without substantial deactivation. 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 concentration of hydrogen sulfide in the gaseous phase should not exceed 0.05 p.s.i.a. and preferably should be less than 0.03 p.s.i.a. 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 in inhibiting effect to at least about 50 p.p.m. of thiophene sulfur (e.g., about 20 p.p.m. of hydrogen sulfide). Where the charge contains less of such 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, especially when subjected to substantially complete vaporization, 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. Accomplishing this by merely passing the initial effluent through a heater and into the second stage 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 catalyst mass or both, and stoppages of this nature call for much cleaning and/or regeneration that reduce the overall operating efficiency. Instead the instant process is concerned with vaporization of the initial effluent in the presence of a flux liquid. 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 is withdrawn 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 temperature 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 to say less than 2 feet per second to minimize the entrainment of droplets therein and a suitable demister is usually provided to catch any traces of entrained liquid in the rising vapors.

The supply of steam to the indirect heater may be manually controlled to maintain a predetermined temperature in the vaporizing chamber as steady as possible, but far better results are usually obtainable in regulating the steam supply in response to the liquid level in the separating chamber according to the invention described and claimed in application Serial No. 238,690 of Richard G. Graven and Vernon O. Bowles filed concurrently herewith. That application also described more fully and claims the feature of injecting hot hydrogen for vaporizing a portion of the liquid hydrogenation effluent.

In brief 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 in-

vention, 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 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 vaporizer pot. This regulation may be exercised either on the quantity of said gas being admitted to the transfer line or on 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 vaporizing or flash chamber. It minimizes or inhibits gum formation at this critical stage of the 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 vaporizer pot 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 re-

actor, 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 concentration in the flux liquid; hence, high circulation rates provide no important advantages.

The concentration of polymer in the circulating flux is dependent on the small but significant proportion 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/second or less. This can be achieved by providing a rea-

sonably 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 when ever 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 vessel. 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 if necessary 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 final 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 refinery 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.

#### EXAMPLE 1

Turning now to the drawing, a freshly-distilled stream of thermally cracked and depentanized gasoline (170–220° 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 valve 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 prolysis 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 cata-

lyst described hereinbefore which has been partially deactivated by a liquid feed containing undesired polymeric materials.

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 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 0.51 percent of chromium in the form of oxides.

The reaction conditions in the first reactor 12 are:

|                                             |                |
|---------------------------------------------|----------------|
| Inlet temperature                           | 115° F.        |
| Outlet temperature                          | 170° F.        |
| Pressure                                    | 730 p.s.i.g.   |
| Hydrogen partial pressure                   | 420 p.s.i.a.   |
| H <sub>2</sub> : liquid feed charging ratio | 1795 s.c.f./b. |
| Liquid space velocity                       | 2.2 v./hr./v.  |
| Catalyst activity indexes:                  |                |
| Hydrogenation                               | 100.           |
| Polymerization                              | <22.           |
| Benzene conversion                          | —              |
| Desulfurization                             | 0.             |

In the first stage reaction the primary reaction is one of the nondestructive hydrogenation of diolefins, especially conjugated diolefins, accomplished 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 vaporizer pot 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 the 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 vaporizer 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, much more is evaporated during passage through line 14 and heater 15, further substantial 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 line 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 at desulfurizing temperatures. 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 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 vaporizer 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 vaporizer 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 vaporizing chamber 18 via conduit 54 to join the hydrogen-rich gas from pipe 32 in line 56 as the charge for the second stage reactor 58. In this passage, the heat exchanger 52 raises the temperature of the overhead effluent to 485° and admixture 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 unique 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 vaporizer 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 of 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.

The second reactor 58 contains a bed of a composite of cobalt and molybdenum sulfides on a gamma alumina of  $\frac{3}{16}$  inch particle 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  $\text{Al}_2\text{O}_3\text{:Mo:Co}$  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 in said effluent in a nondestructive manner with no substantial saturation of aromatic compounds. The reaction conditions in the second stage reactor are as follows:

|                                          |                |
|------------------------------------------|----------------|
| Inlet temperature                        | 515°.          |
| Outlet temperature                       | 535°.          |
| Total pressure                           | 685 p.s.i.g.   |
| $\text{H}_2$ partial pressure            | 335 p.s.i.a.   |
| Total $\text{H}_2$ charged               | 3350 s.c.f./b. |
| Space velocity calculated on liquid feed | 1.7 v./Hr./v.  |
| Catalysts activity indexes:              |                |
| Desulfurization                          | 98+.           |
| 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 the reactor charges and effluents of column 4 with column 5 in Table I and also column 6 with 7. The latter two indicate that a minor hydrogenation of diolefins is completed in the final reactor along with the principal hydrogenation that saturates substantially all 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.

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 meet with any make-up gas drawn from supply conduit 4 via valved line 92 that also may require scrubbing to remove excessive hydrogen sulfide. 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  $\text{H}_2\text{S}$  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

Table I

| Stream                           | 1<br>Gasol.<br>Feed | 2<br>Fresh<br>$\text{H}_2$ -Rich<br>Gas | 3<br>Total<br>$\text{H}_2$ -Rich<br>Gas | 4<br>First<br>Reactor<br>Charge | 5<br>First<br>Reactor<br>Effluent | 6<br>Final<br>Reactor<br>Charge | 7<br>Final<br>Reactor<br>Effluent | 8<br>H.P.<br>Sep. Off<br>Gas | 9<br>Stabi-<br>lizer<br>Off Gas | 10<br>Stabi-<br>lized<br>Liquid |
|----------------------------------|---------------------|-----------------------------------------|-----------------------------------------|---------------------------------|-----------------------------------|---------------------------------|-----------------------------------|------------------------------|---------------------------------|---------------------------------|
| Flow, lbs./Hour                  | 28,220              | 2,520                                   | 14,020                                  | 35,230                          | 35,230                            | 39,680                          | 39,680                            | 1,860                        | 920                             | 25,400                          |
| Flow, c.f./Min. <sup>1</sup>     |                     | 42                                      | 213                                     |                                 |                                   | 452                             | 478                               | 240                          | 19                              |                                 |
| 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 <sup>2</sup>   | 0                   |                                         |                                         | 0                               | 4                                 | 91.5                            |                                   |                              |                                 |                                 |
| Organic S, p.p.m. <sup>2</sup>   | 450                 |                                         |                                         | 450                             | 450                               | 450                             | 10                                |                              |                                 | 10                              |
| Mols per Hour:                   |                     |                                         |                                         |                                 |                                   |                                 |                                   |                              |                                 |                                 |
| $\text{H}_2$                     |                     | 195.0                                   | 961.0                                   | 480.5                           |                                   |                                 |                                   |                              |                                 |                                 |
| $\text{C}_1$                     |                     | 79.5                                    | 501.2                                   | 250.6                           |                                   |                                 |                                   |                              |                                 |                                 |
| $\text{C}_2$                     |                     | 20.1                                    | 68.3                                    | 34.2                            |                                   |                                 |                                   |                              |                                 |                                 |
| $\text{H}_2\text{S}$ (in p.p.m.) |                     | (10)                                    |                                         |                                 |                                   |                                 |                                   |                              |                                 |                                 |
| $\text{C}_3$                     |                     | 4.2                                     | 10.1                                    | 5.1                             |                                   |                                 |                                   |                              |                                 |                                 |
| $\text{C}_4$                     |                     | 0.9                                     | 1.3                                     | 0.7                             |                                   |                                 |                                   |                              |                                 |                                 |
| $\text{C}_5$ Saturates           | 0.9                 | 1.8                                     | 2.3                                     | 1.2                             |                                   |                                 |                                   |                              |                                 |                                 |
| $\text{C}_5$ Unsaturates         | 3.4                 |                                         |                                         | 3.5                             |                                   |                                 |                                   |                              |                                 |                                 |
| $\text{C}_6$ Saturates           | 29.7                |                                         | 3.1                                     | 31.9                            |                                   |                                 |                                   |                              |                                 |                                 |
| $\text{C}_6$ Unsaturates         | 29.7                |                                         |                                         | 30.6                            |                                   |                                 |                                   |                              |                                 |                                 |
| Benzene                          | 270.4               |                                         | 13.6                                    | 277.2                           |                                   |                                 |                                   |                              |                                 |                                 |
| Toluene                          | 3.5                 |                                         | 0.1                                     | 3.6                             |                                   |                                 |                                   |                              |                                 |                                 |
| Other $\text{C}_{7+}$            | 16.1                |                                         |                                         | 15.3                            |                                   |                                 |                                   |                              |                                 |                                 |
| Total, Mols/Hr.                  | 353.7               | 300.0                                   | 1560.9                                  | 1134.2                          |                                   |                                 |                                   |                              |                                 |                                 |

<sup>1</sup> Measured under actual process conditions.

<sup>2</sup> Based on weight of original liquid feed.

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

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 of 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 column. 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 glycols, 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 temperature. 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 reformat 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 flash chamber 18 from the time the reformat 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

reformat 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

The process of Example 1 is repeated using the same feed, equipment and reaction conditions except as otherwise specified herein. The catalysts are of identical composition with those described in Example 1 except that the data tabulated hereinafter represents steady state conditions after operating for only five days with fresh new catalysts in both reactors.

Table II.

#### OPERATING CONDITIONS

|                                                         |      |
|---------------------------------------------------------|------|
| Flow rates—b./d.:                                       |      |
| Pyrolysis liquid charge                                 | 3060 |
| First reactor outlet                                    | 2900 |
| Flux oil circulation                                    | 710  |
| Spent flux                                              | 74   |
| Stabilizer feed                                         | 3090 |
| Circulating gas (72.5% H <sub>2</sub> )—m.s.c.f./h.:    |      |
| From caustic & water scrubber                           | 742  |
| To first-stage (Pd) reactor                             | 341  |
| To furnace 26                                           | 336  |
| To fuel line 84                                         | 65   |
| To transfer line 34                                     | 218  |
| To transfer line 32                                     | 118  |
| Make-up gas (76% H <sub>2</sub> )                       | 98.8 |
| Pressures—p.s.i.g.:                                     |      |
| Recycle gas compressor outlet                           | 730  |
| Recycle gas compressor inlet                            | 630  |
| First reactor inlet                                     | 700  |
| First reactor—H <sub>2</sub> partial pressure—p.s.i.a.  | 405  |
| Vaporizer pot                                           | 690  |
| Second reactor inlet                                    | 685  |
| Second reactor—H <sub>2</sub> partial pressure—p.s.i.a. | 330  |
| Temperatures—° F.:                                      |      |
| First reactor, inlet                                    | 103  |
| First reactor, outlet                                   | 197  |
| First reactor, ΔT                                       | 94   |
| Second reactor, inlet                                   | 486  |
| Second reactor, outlet                                  | 490  |
| Second reactor, ΔT                                      | 4    |
| Gas furnace outlet 28                                   | 630  |
| Outlet of heater 15                                     | 350  |
| Vaporizer pot inlet                                     | 356  |
| Circulating flux oil in line 16                         | 350  |
| Space velocities—LHSV:                                  |      |
| First reactor                                           | 2.88 |
| Second reactor                                          | 2.24 |

In comparison with Example 1, the temperatures listed immediately above demonstrate a considerably larger temperature rise in passing through the first reactor and a considerably smaller exotherm in the second reactor. This means that a distinctly greater degree of hydrogenation is taking place in the first reactor and less in the second than is the case in Example 1 where a catalyst of somewhat impaired activity is used in the first reactor.

The following properties of several streams are established by analyses:

Table III

| Characteristics  | Charge | First Reactor Effluent | Spent Flux | Stabilizer Bottoms (Product) |
|------------------|--------|------------------------|------------|------------------------------|
| Gum, mg./100 ml. | 5      | 1.5                    | 53         | 1                            |
| Specific Gravity | 0.828  | 0.830                  | 0.837      | 0.824                        |
| Unsaturation:    |        |                        |            |                              |
| Bromine No.      | 18.2   | 2.9                    |            | Nil                          |
| Diene No.        | 9.9    | Nil                    |            | Nil                          |
| Sulfur, p.p.m.   | 39     |                        |            | 1.1                          |

## 21

The results in Table III for catalysts with an age of five days amount to reductions of 100% in Diene Number and 84% in Bromine Number for the product of the first reactor based on the values for the feed stock. Reductions of 85 and 55% respectively after 20 days of operation, and 80 and 50% reductions respectively after a total of 75 days are obtained in operating the initial reactor under the same reaction conditions. It is estimated that the first stage reactor can be operated for a period of at least 6 months before regeneration of the catalyst is likely to be required to maintain a diolefin reduction of 50% while keeping the charge temperature below 250° F.

## EXAMPLE 3

A pilot plant is operated under the conditions generally similar to those in Example 2 in hydrogenating a pyrolysis gasoline of the same type using undiluted hydrogen instead of a mixture of hydrogen and light hydrocarbons as the reactant gas. The recirculation of a liquid flux is omitted and unvaporized liquid effluent from the first reactor is drained intermittently from the relatively large flash vaporization chamber in amounts equal to 12% of the liquid feed. The catalysts are the same except that the data listed hereinafter are illustrative of catalysts on-stream for 11 days.

Table IV

| Operating Conditions                      | 1st Reactor | 2nd Reactor |
|-------------------------------------------|-------------|-------------|
| Space Velocity, LHSV                      | 4.0         | 2.0         |
| Hydrogen Circulation Rate, s.c.f./b       | 1,500       | 3,400       |
| H <sub>2</sub> Partial Pressure, p.s.i.a. | 450         | 450         |
| Total Pressure, p.s.i.g.                  | 500         | 685         |
| Inlet Temperature, ° F                    | 136         | 500         |
| Average Bed Temperature, ° F              | 147         | 500         |
| Peak Temperature, ° F                     | 158         | 565         |
| Vaporization of Liquid Feed, percent      | About 15    |             |

Routine analytical methods are employed in determining the following properties of certain streams.

Table V

| Characteristics          | Charge  | 1st Reaction Product | 2nd Reaction Product |
|--------------------------|---------|----------------------|----------------------|
| Distillation Range, ° F  | 158-218 | 158-204              |                      |
| Gum, mg./100 ml.         | 19      | 8                    |                      |
| Total Sulfur, p.p.m.     | 25      | 28                   |                      |
| Thiophene Sulfur, p.p.m. |         |                      | About 1.0            |
| Diene No.                | 18      | 7                    | Nil                  |
| Bromine No.              | 22      | 15                   | Nil                  |

## EXAMPLE 4

Example 3 is repeated using a lower end point stock of the same type and a slightly lower temperature in the first reactor. The equipment and both catalysts are identical with those of Example 3, except that the operating age of the catalysts now totals 20 days.

Table VI

| Operating Conditions                      | 1st Reactor | 2nd Reactor |
|-------------------------------------------|-------------|-------------|
| Space Velocity, LHSV                      | 4.0         | 2.0         |
| Hydrogen Circulation, s.c.f./b            | 1,500       | 3,400       |
| H <sub>2</sub> Partial Pressure, p.s.i.a. | 450         | 330         |
| Total Pressure, p.s.i.g.                  | 500         | 475         |
| Inlet Temperature, ° F                    | 118         | 500         |
| Average Bed Temperature, ° F              | 130         | 550         |
| Peak Temperature, ° F                     | 143         | 570         |
| Vaporization of Liquid Feed, Percent      | About 15    |             |

## 22

The following characteristics are determined by conventional tests.

Table VII

| Characteristics          | Charge  | 1st Reaction Product | 2nd Reaction Product |
|--------------------------|---------|----------------------|----------------------|
| Distillation Range, ° F  | 160-200 | 159-200              |                      |
| Gum, mg./100 ml.         | 10      | 38                   |                      |
| Total Sulfur, p.p.m.     | 23      | 22                   |                      |
| Thiophene Sulfur, p.p.m. |         |                      | About 1.0            |
| Diene No.                | 15      | 7                    | Nil                  |
| Bromine No.              | 19      | 14                   | Nil                  |

## EXAMPLE 5

The liquid product of the first reactor of Example 3, that is partially hydrogenated pyrolysis gasoline, is pumped through a laboratory Erdco coker with an aluminum insert therein at the rate of 6.1 pounds/hour. With the inlet end of the insert at ambient temperature, the liquid is heated to 300° while passing over the aluminum insert and the outlet is maintained at that temperature for 1 hour. A substantial proportion but not all of the charge evaporates during this interval in which a constant pressure of 125 p.s.i.g. is maintained on the apparatus. Upon removal of the aluminum insert, a slight hazy white deposit is noted on the material. The whitish deposit amounts to 0.13 gram or 47 p.p.m. on the basis of liquid charged.

The above experiment is repeated charging the same liquid at 5.9 pounds/hour with the pressure on the coker reduced to 40 p.s.i.g. All of the liquid therein evaporates to dryness under these conditions. The aluminum insert is now found to be coated with a heavy brown layer of polymeric material from the liquid. In removing the insert from the apparatus a substantial part of this deposit is lost, yet the remainder is found to weigh 2.6 grams or 970 p.p.m. based on the deposit charged.

Even though the partial hydrogenation of pyrolysis gasoline is believed to have a substantial stabilizing effect against polymerization, it is apparent from these results that vaporization of even the partially hydrogenated product must be carefully controlled and carried out so that the evaporation to dryness is avoided in order to prevent plugging the equipment with deposits of polymeric solids which can increase more than twenty-fold from this cause.

The detailed examples given hereinabove 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 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. For simplicity and to provide comparative results, the same catalysts are employed in all of the detailed examples; but the invention is not limited to such catalysts for a wide variety of other known hydrogenation and desulfurization catalysts may be used. Accordingly, the present invention is not to be considered as limited in any respect other than the recitals of the appended claims.

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 substantially in the liquid phase and hydrogen through an initial hydrogenation zone in contact with a porous solid hydrogenation catalyst of high hydrogenation activity and low polymerization activity while controlling hydrogenating conditions in said zone including hydrogen partial pressure within the range of

about 200–800 p.s.i.a., hourly space velocity within the range of about 0.2–15.0 based on the volume of liquid feed, the hydrogen charge within the range of about 500–5000 s.c.f./b. of liquid feed and feed temperature within the broad range of about 75–300° F., said hydrogenating conditions being regulated 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 amount of said effluent is in the liquid phase, effecting controlled vaporization of a portion of the liquid phase of said hydrogenation effluent, passing hydrogen together with gaseous material derived from vaporization step through a subsequent conversion zone in contact with a porous solid conversion catalyst of at least moderate hydrogenation activity and high desulfurization activity at a substantially higher average temperature than in said initial zone while controlling conversion conditions in said conversion zone including hydrogen partial pressure within the range of about 200–800 p.s.i.a., hourly space velocity within the range of about 0.2–6.0 based on the volume of said liquid feed, the total hydrogen charge within the range of about 500–10,000 s.c.f./b. of said liquid feed and inlet temperature within the wide range of about 350–700° F., said conversion conditions being regulated to produce a substantially desulfurized conversion effluent having a substantially 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 substantially in the liquid phase and hydrogen through an initial hydrogenation zone in contact with a porous solid hydrogenation catalyst of high hydrogenation activity and low polymerization activity while controlling hydrogenating conditions in said zone including hydrogen partial pressure within the range of about 200–800 p.s.i.a., hourly space velocity within the range of about 0.2–15.0 based on the volume of liquid feed, the hydrogen charge within the range of about 500–5000 s.c.f./b. of liquid feed and feed temperature within the broad range of about 75–300° F., said hydrogenating conditions being regulated 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 amount of said effluent is in the liquid phase, effecting controlled vaporization of a portion of the liquid phase of said hydrogenation effluent and separation of the gaseous phase thereof in the presence of a substantial amount of liquid flux, passing hydrogen together with gaseous material derived from said vaporization step through a subsequent conversion zone in contact with a porous solid conversion catalyst of at least moderate hydrogenation activity and high desulfurization activity at a substantially higher average temperature than in said initial zone while controlling conversion conditions in said conversion zone including hydrogen partial pressure within the range of about 200–800 p.s.i.a., hourly space velocity within the range of about 0.2–6.0 based on the volume of said liquid feed, the total hydrogen charge within the range of about 500–10,000 s.c.f./b. of said liquid feed and inlet temperature within the wide range of about 350–700° F., said conversion conditions being regulated to produce a substantially desulfurized conversion effluent having a substantially lower Bromine Number than said liquid feed.

3. 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 substantially in the liquid phase and hydrogen through an initial hydrogenation zone in contact with a porous solid hydrogenation catalyst of high hydrogenation activity and low polymerization activity while controlling hydrogenating conditions in said zone including hydrogen partial

pressure within the range of about 200–800 p.s.i., hourly space velocity within the range of about 0.2–15.0 based on the volume of liquid feed, the hydrogen charge within the range of about 500–5000 s.c.f./b. of liquid feed and feed temperature within the broad range of about 75–300° F., said hydrogenating conditions being regulated 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 an amount equal to at least about 20% of the liquid feed remains in the liquid phase, effecting controlled vaporization of a portion of said hydrogenation effluent and separation of the gaseous phase thereof in the presence of a liquid flux in an amount equal to at least about 5% of said liquid feed, with drawing said liquid flux from said vaporization step in an amount equal to at least about 0.5% of said liquid feed, passing hydrogen together with gaseous material derived from said vaporization step through a subsequent conversion zone in contact with a porous solid conversion catalyst of at least moderate hydrogenation activity and high desulfurization activity at a substantially higher average temperature than in said initial zone while controlling conversion conditions in said conversion zone, including hydrogen partial pressure within the range of about 200–800 p.s.i.a., hourly space velocity within the range of about 0.2–6.0 based on the volume of said liquid feed, the total hydrogen charge within the range of about 500–10,000 s.c.f./b. of said liquid feed and inlet temperature within the wide range of about 350–700° F., said conversion conditions being regulated to produce a conversion effluent from said conversion zone with a normally liquid fraction having a Bromine Number less than about 4 and an organic sulfur content below about 20 p.p.m.

4. A process according to claim 3 in which said liquid feed is rich in aromatic hydrocarbons and boils within the range of about 140–275° F.

5. A process according to claim 3 in which said initial catalyst has a hydrogenation activity index of at least about 40 and a polymerization activity index less than about 35 and said conversion catalyst has a desulfurization activity index of at least about 80.

6. A process according to claim 3 in which said liquid feed temperature is maintained within the narrow range of about 75–190° F. while said initial catalyst is fresh and then 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 is maintained with the limited range of about 400–550° F. while said conversion catalyst is fresh and then increased within said wide range to maintain said organic sulfur content and Bromine Number in said conversion effluent fraction as the activity of the conversion catalyst decreases with continued use.

7. A process according to claim 3 in which the hydrogen sulfide partial pressure in said initial hydrogenation zone is maintained below about 0.05 p.s.i.a.

8. A process according to claim 3 in which said hydrogenation effluent is retained in the liquid state in an amount equal to between about 1 and 10% of said liquid feed in said controlled vaporization which is further regulated within said range to increase the quantity of said liquid effluent when the concentration of polymeric hydrocarbons therein increases and to decrease the quantity of said liquid effluent when the concentration of polymeric hydrocarbons therein decreases.

9. A process according to claim 3 in which the products of said controlled vaporization step are separated into gaseous and liquid phases in an enlarged separation zone and an amount of liquid at least equal to about 1.0% of said liquid feed and containing polymeric hydrocarbons is withdrawn at least intermittently from said separation zone and from said process.

10. A process according to claim 3 in which said hydrogenation effluent is retained in the liquid state in an

amount equal to between about 1 and 10% of said liquid feed in said controlled vaporization which is further regulated within said range to increase the quantity of said liquid effluent when the concentration of polymeric hydrocarbons therein increases and to decrease the quantity of said liquid effluent when the concentration of polymeric hydrocarbons therein decreases, separating the products of said vaporization into gaseous and liquid phases in an enlarged separation zone and withdrawing said liquid phase from said separation zone and from said process at least intermittently at an average rate equal to the rate of said liquid retention in order to minimize the accumulation of polymeric material therein.

11. A process according to claim 3 in which said controlled vaporization is effected in the presence of a quantity of circulating liquid flux at least equal to 10% of said liquid feed and capable of dissolving hydrocarbon gums.

12. A process according to claim 3 in which said controlled vaporization is effected in the presence of a quantity of circulating liquid flux at least equal to 10% of said liquid feed, said flux containing predominantly hydrocarbons including at least 15% of aromatic hydrocarbons.

13. A process according to claim 3 in which said controlled vaporization is effected in the presence of a liquid flux recirculating at a rate equal to at least 10% of that of said liquid feed and said flux comprises a portion of the less volatile fraction obtained from said hydrogenation effluent.

14. A process according to claim 3 in which said controlled vaporization is effected in the presence of a liquid hydrocarbon flux circulating at a rate equal to at least 10% of that of said liquid feed and said hydrogenation effluent is retained in the liquid state and withdrawn from the process in an amount equal to between about 1 and 10% of said liquid feed.

15. A process according to claim 3 in which said controlled vaporization is effected in the presence of a liquid hydrocarbon flux circulating at a rate equal to at least about 10% of that of said liquid feed, said hydrogenation effluent is retained in the liquid state in an amount equal to between about 1 and 10% of said liquid feed and said vaporization is further regulated within said range of retention of liquid effluent to increase the quantity of said liquid effluent when the concentration of polymeric hydrocarbons therein increases and to decrease the quantity of said liquid effluent when the concentration of polymeric hydrocarbons therein decreases.

16. A process according to claim 3 in which said controlled vaporization is effected by heating by means including introducing into said hydrogenation effluent a recirculating liquid flux at a substantially higher temperature than said hydrogenation effluent and at a rate equal to at least 10% of that of said liquid feed.

17. A process according to claim 3 in which said controlled vaporization is effected in a restricted transfer conduit in the presence of a liquid flux recirculating at a rate equal to at least 10% of that of said liquid feed and the resulting gaseous phase is separated from the flux in an enlarged separation zone.

18. A process according to claim 3 in which a major part of said controlled vaporization is effected in a restricted transfer conduit wherein a recirculating liquid flux is introduced into said hydrogenation effluent at a rate equal to at least 10% of that of said liquid feed, and the resulting gaseous phase is separated from said flux in an enlarged separation zone.

19. A process according to claim 3 in which a substantial part of said controlled vaporization is effected in a restricted transfer conduit by heating by means including introducing a recirculating liquid flux into said hydrogenation effluent at a substantially higher temperature than that of said hydrogenation effluent and at a rate equal to at least 10% of that of said liquid feed, and the

resulting gaseous phase is separated from said flux in an enlarged separation zone.

20. A process according to claim 19 in which a major portion of said flux is continuously recirculated from said enlarged zone to said conduit and a minor portion thereof is withdrawn at least intermittently from the process to minimize the accumulation of polymeric material in said flux.

21. A continuous process for the selective nondestructive hydrogenation of a liquid hydrocarbon feed boiling below about 500° F. which is rich in aromatic hydrocarbons and contains olefins, diolefins and sulfur compounds which comprises passing said feed substantially in the liquid phase and hydrogen through an initial hydrogenation zone in contact with a porous solid hydrogenation catalyst of high hydrogenation activity and low polymerization activity while controlling hydrogenating conditions in said zone including hydrogen partial pressure within the range of about 300–600 p.s.i.a., hourly space velocity within the range of about 0.5–8.0 based on the volume of liquid feed, the hydrogen charge within the range of about 1200–3000 s.c.f./b. of liquid feed and feed temperature within the broad range of about 75–250° F., said hydrogenating conditions being regulated to provide a hydrogenation effluent from said zone in which the Bromine Number of the normally liquid fraction thereof is at least about 25% below that of the liquid feed and at least about 60% of the diolefins have been at least partially saturated and in which an amount equal to at least about 60% of the liquid feed remains in the liquid phase, effecting controlled vaporization of a substantial portion of said liquid hydrogenation effluent and separation of the gaseous phase thereof in the presence of a liquid hydrocarbon effluent and separation of the gaseous phase thereof in the presence of a liquid hydrocarbon flux in an amount equal to at least about 10% of said liquid feed, thereafter withdrawing liquid hydrogenation effluent from said vaporization step in an amount equal to at least about 1% of said liquid feed, passing hydrogen together with gaseous material derived from said vaporization step through a subsequent hydrogen treating zone in contact with a porous solid treating catalyst of at least moderate hydrogenation activity and high desulfurization activity at a substantially higher average temperature than in said initial zone while controlling treating conditions in said treating zone including hydrogen partial pressure within the range of about 300–600 p.s.i.a., hourly space velocity within the range of about 0.5–4.0 based on the volume of said liquid feed the total hydrogen charge within the range of about 2000–5000 s.c.f./b. of said liquid feed and inlet temperature within the wide range of about 400–650° F., said treating conditions being regulated to produce a treated effluent from said treating zone with a normally liquid fraction having a Bromine Number less than about 2 and an organic sulfur content below about 15 p.p.m.

22. A process according to claim 1 in which said initial catalyst has a hydrogenation activity index of at least about 40 and a polymerization activity index less than about 35 and said treating catalyst has a desulfurization activity index of at least about 80.

23. A process according to claim 21 in which said liquid feed temperature is maintained within the narrow range of about 75–190° F. while said initial catalyst is fresh and then 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 is maintained within the limited range of about 400–550° F. while said treating catalyst is fresh and then increased within said wide range to maintain said sulfur content and Bromine Number in said treated effluent fraction as the activity of said treating catalyst decreases with continued use.

27

24. A process according to claim 21 in which the hydrogen sulfide partial pressure in said initial zone is maintained below about 0.03 p.s.i.a.

25. A process according to claim 21 in which said hydrogenation catalyst comprises finely-divided palladium supported on an inert carrier and said treating catalyst comprises a sulfided composite of cobalt and molybdenum supported on an inert carrier.

26. A process according to claim 21 in which the Bromine Number of said normally liquid fraction of the initial hydrogenation effluent is between about 25 and 95% below that of said liquid feed.

28

## References Cited by the Examiner

## UNITED STATES PATENTS

|           |         |                    |         |
|-----------|---------|--------------------|---------|
| 2,952,625 | 9/1960  | Kelley et al. .... | 208—254 |
| 3,051,647 | 8/1962  | White .....        | 208—255 |
| 3,075,917 | 1/1963  | Kronig et al. .... | 208—255 |
| 3,108,947 | 10/1963 | Stijntjes .....    | 208—255 |

PAUL M. COUGHLAN, *Primary Examiner*.ALPHONSO D. SULLIVAN, *Examiner*.