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HYDROREFINING OF COKE-FORMING HYDROCARBON DISTILLATES

Ernest L. Pollitzer, Skokie, Ill., assignor to Universal Oil Products Company, Des Plaines, Ill.

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ABSTRACT OF THE DISCLOSURE

A process for hydrorefining sulfurous hydrocarbon distillates containing mono-olefinic, di-olefinic and aromatic hydrocarbons. Through the use of particular catalytic composites containing metallic components from Group VII–B, having an atomic number greater than 25, and the noble metals of Group VIII, increased selectivity and stability of operation is attained. The selectivity is most noticeable with respect to the retention of aromatics, and in hydrogenating conjugated di-olefinic and mono-olefinic hydrocarbons.

APPLICABILITY OF INVENTION

In the present specification and appended claims, the terms, "hydrocarbon," "hydrocarbon fractions," "hydrocarbon distillates," and "hydrocarbon mixtures," are used interchangeably to connote synonymously various mixtures of hydrocarbons resulting from diverse conversion processes. Such processe include the catalystic and/or thermal cracking of petroleum, sometimes referred to as pyrolysis, the destructive distillation of wood or coal, shale-oil retorting, etc. The resulting hydrocarbon distillate fractions frequently contain impurities which must necessarily be removed before the distillate fractions are suitable for their intended use, or which when removed, enhance the value of the distillate fraction for further processing. These impurities include sulfurous compounds, nitrogenous compounds, oxygenated compounds, all of which cause the hydrocarbon distillates to exhibit corcorsive tendencies, and be foul-smelling.

In addition to the aforementioned contaminating influences, the hydrocarbon distillates generally contain appreciable quantities of unsaturated hydrocarbons, including mono-olefinic, di-olefinic (including conjugated di-olefins) and aromatic hydrocarbons. The mono-olefinic and di-olefinic hydrocarbons induce the coke-forming characteristics of the hydrocarbon distillate, as do the styrenes, and, when subjected to hydrotreating for the purpose of removing the contaminating influences, there is encountered difficulty in effecting a desired degree of reaction due to the formation of coke and other carbonaceous material. The deposition of coke appears to be an inherent result of the necessity to effect the hydrotreating process at elevated temperatures above about 500° F. in order to desulfurize. Various heaters and other appurtenances of the conversion zone experience heavy coking which appears as a formation of solid, highly carbonaceous material resulting from the thermal reaction of the unstable, conjugated di-olefins and styrenes within the distillates being charged to the unit. In addition, polymerization and co-polymerization reactions are effected within the hydrotreating reaction zone, and to the extent that the catalytic composite disposed therein becomes shielded from the material being processed.

As hereinbefore set forth, coke-forming hydrocarbon distillates are usually those resulting from prior conversion treatments, such as catalytic or thermal cracking, or destructive distillation. In the interest of simplicity, the following discussion will be principally directed toward processing the hydrocarbon distillate resulting from a

naphtha pyrolysis unit designed for the production of normally gaseous olefinic material such as ethylene, propylene, butadiene, etc. The so-called pyrolysis naphtha co-product is available in relatively large quantities, but generally requires a hydrotreating treatment for the purpose of enhancing the possibilities of further usefulness. In many instances, the pyrolysis naphtha co-product will not contain excessive quantities of sulfurous and/or nitrogenous compounds, but will consist of detrimental amounts of mono-olefins and di-olefins, such that the subsequent use of the distillate is prohibited. For example, in a thermal cracking process designed primarily for ethylene production, a full boiling range hydrocarbon distillate is produced, which distillate may contain less than 1000 p.p.m. each of sulfur and/or nitrogen, but will generally contain sufficient olefinic hydrocarbons to indicate a bromine number of the order of at least about 25.0, and often more, and di-olefins in an amount to indicate a diene value of the order of about 20.0 or more.

In general, the pyrolysis reaction is effected in the absence of a catalytic composite, at elevated temperatures in the presence of a diluent such as superheated steam. Depending upon the physical and/or chemical characteristics of the charge stock, as well as the specific pyrolysis conditions being maintained, the product effluent from the cracking zone comprises light olefinic hydrocarbons, including ethylene, propylene, butylene, butadiene, etc., a pyrolysis naphtha fraction containing pentanes, hexanes and heavier hydrocarbons boiling up to a temperature of about 300° F. to about 400° F., and also including aromatics, mono-olefinic hydrocarbons, di-olefinic hydrocarbons, styrenes and sulfurous compounds. Visualized as exemplary of suitable charge stocks to the present process are: a pyrolyis naphtha having a gravity of 35.1° API, containing 1100 p.p.m. by weight of sulfur, having an end boiling point of 350° F., a bromine number of 43.0 and a diene value of 40.0; a 400° F. (end boiling point) naphtha having a gravity of 43.5° API, containing 500 p.p.m. by weight of sulfur, and having a bromine number of 74.0 and a diene value of about 80.0; and, a C_4/C_5 concentrate having a gravity of 76.7° API, containing 500 p.p.m. by weight of sulfur, and having a bromine number of about 200.0 and a diene value of about 230.0. Since the pyrolysis naphtha fractions are heavily contaminated, it is usually a common practice to hydrotreat for saturation of the olefins and/or di-olefins, while destructively converting the sulfurous compounds into hydrogen sulfide and hydrocarbons. As hereinbefore stated, di-olefinic hydrocarbons present particular difficulty in the operation of the hydrotreating facilities by way of extensive equipment fouling and catalyst deactivation. Attempts are often made to improve the on-stream efficiency of the hydrotreating process, by either promoting the polymerization prior to the hydrotreating step, or by utilizing operating techniques which tend to minimize or inhibit polymer formation. However, none of these aproaches are successful in overcoming the fouling difficulty to the extent that the process enjoys an acceptable degree of stability.

Of greater significance, perhaps, is the lack of selectivity in prior art processes for hydrotreating coke-forming hydrocarbon fractions. For example, the hydrogenation of the conjugated di-olefinic hydrocarbons and styrenes may not end with the conversion thereof to the mono-olefins and alkyl benzenes, but will frequently continue to complete saturation. Similarly, the aromatic hydrocarbons initially present in the pyrolysis naphtha fraction suffer degradation as a result of complete, or partial hydrogenation. Such non-selectivity obviously results in a decrease of desirable products in thus-treated product effluent. In accordance with the present process, through the use of particular catalytic composites and operating

conditions, a coke-forming hydrocarbon distillate is selectively hydrogenated and desulfurized with minimum polymer formation and minimum degradation of desired constituents.

OBJECTS AND EMBODIMENTS

A principal object of the present invention is to effect the saturation of di-olefinic hydrocarbons, and the desulfurization of sulfurous compounds, present in coke-forming hydrocarbon distillates. A corollary objective is to provide stability and selectivity in a process for stabilizing coke-forming naphtha fractions.

A specific object of my invention is to hydrogenate di-olefinic hydrocarbons in a pyrolysis naphtha co-product, without degradation of the mono-olefins and aromatic hydrocarbons.

Another specific object is to desulfurize a sulfurous hydrocarbon distillate, containing aromatic and mono-olefinic hydrocarbons, to provide a substantially sulfur-free aromatic concentrate.

Therefore, in one embodiment, my invention provides a process for hydrorefining an unsaturated, coke-forming hydrocarbon distillate, containing mono-olefinic and di-olefinic hydrocarbons, which process comprises reacting said distillate and hydrogen in a first catalytic reaction zone at a temperature less than about 500° F., in contact with a catalytic composite of an alumina-containing inorganic oxide, a Group VIII noble metal component, a Group VII–B metal component, having an atomic number greater than 25, and an alkali-metal component, increasing the temperature of the resulting first reaction zone effluent to a level above about 800° F., reacting the thus-heated product effluent with hydrogen in a second catalytic reaction zone, in contact therein with a catalytic composite of an alumina-containing refractory inorganic oxide, a Group VIII noble metal component and a Group VII–B metallic component, having an atomic number greater than 25, and separating the resulting second reaction zone effluent to recover said hydrocarbon distillate substantially free from conjugated di-olefinic hydrocarbons.

In another embodiment, my invention provides a process for desulfurizing a sulfurous hydrocarbon distillate containing mono-olefinic hydrocarbons and aromatics, which process comprises reacting said distillate with hydrogen, at a temperature above about 800° F., in contact with a catalytic composite of an alumina-containing refractory inorganic oxide, a Group VIII noble metal component and a Group VII–B metal component, having an atomic number greater than 25.

In another embodiment, the present invention relates to a process for hydrogenating a coke-forming hydrocarbon distillate containing di-olefinic and mono-olefinic hydrocarbons, and aromatics, which process comprises reacting said distillate with hydrogen, at a temperature below about 500° F., in contact with a catalytic composite of an alumina-containing refractory inorganic oxide, a Group VIII noble metal component, an alkali metal component and a Group VII–B metal component having an atomic number greater than 25, and recovering an aromatic/mono-olefinic hydrocarbon concentrate substantially free from di-olefinic hydrocarbons.

Other embodiments of my invention involve preferred processing techniques and operating conditions, as well as the catalytic composites for utilization in the two catalytic reaction zones. With respect to the latter, it is preferred to utilize a catalytic composite capable of selectively hydrogenating conjugated di-olefinic hydrocarbons to mono-olefinic hydrocarbons, in a hydrocarbon charge stock also containing sulfurous compounds, aromatic hydrocarbons, and mono-olefinic hydrocarbons. In one operating technique, at least a portion of the second catalytic reaction zone effluent is recycled to combine with the fresh hydrocarbon distillate in an amount to result in a combined liquid feed containing a controlled weight percent of the

reactive dienes and styrenes. The preferred catalytic composite, for utilization in the second catalytic reaction zone, is a composite of alumina, platinum and rhenium.

SUMMARY OF INVENTION

As hereinbefore set forth, the purpose of the present invention is to provide a highly selective and stable process for hydrogenating coke-forming hydrocarbon distillates. As utilized herein, the term "hydrogenating" is intended to be synonymous with "hydrotreating" and "hydrorefining." In essence, this purpose is accomplished through the use of a fixed-bed catalytic reaction system.

In accordance with my invention, there exist two separate, desirable routes for the treatment of coke-forming distillates, for example, a pyrolysis naphtha by-product. One such route is directed toward a product suitable for use in certain gasoline blending. With this as the desired object, the process can be effected in a single stage, or reaction zone, using the catalytic composite hereinafter specifically described as the first-stage catalyst. The desired, and attainable selectivity in this instance resides primarily in the hydrogenation of highly reactive double bonds. In the case of conjugated di-olefins, the selectivity afforded restricts the hydrogenation to produce mono-olefins, and, with respect to styrenes, the hydrogenation is inhibited to produce alkyl benzenes without "ring" saturation. Such hydrogenation selectivity is accomplished with a minimum of polymer formation either to "gums," or polymers of lower molecular weight which would necessitate re-running of the product before blending to gasoline would be feasible.

Other advantages of restricting the hydrogenation of the conjugated di-olefins and styrenes include: lower hydrogen consumption, lower heat of reaction and a higher octane rating gasoline boiling range product effluent. Also, non-conjugated di-olefins, such as 1,5 normal hexadiene are not unusually offensive in suitable inhibited gasolines, in some locales, and will possibly not react in this first stage. Some fresh charge stocks are sufficiently low in mercaptan sulfur content that direct gasoline blending may be considered. A mild treatment for mercaptan sulfur removal might be necessary. Such considerations are generally applicable to foreign markets, particularly European, where olefinic and sulfur-containing gasolines are not so critical.

It should be noted that the sulfurous compounds, and the mono-olefins, whether virgin or products of diolefin partial saturation, are unchanged in the single, or first-stage reaction zone. Where, however, the desired end result is aromatic hydrocarbon retention, intended for subsequent extraction, the two-stage route is required. The mono-olefins must be substantially saturated in the second stage to facilitate aromatics extraction by way of currently known and utilized methods. Thus, the desired, necessary hydrogenation involves saturation of the mono-olefins, as well as sulfur removal, the latter required for an acceptable ultimate aromatic product. Attendant upon this is the necessity to avoid even partial saturation of aromatic nuclei.

With erspect to one preferred catalytic composite, its principal function involves the selective hydrogenation of conjugated di-olefinic hydrocarbons to mono-olefinic hydrocarbons, rather than completely to paraffinic hydrocarbons. This particular catalytic composite possesses unusual stability notwithstanding the presence of large quantities of sulfurous compounds in the fresh hydrocarbon charge stock. The catalytic composite is hereinafter described in greater detail. Briefly, however, the catalyst is a composite of an alumina-containing refractory inorganic oxide, a Group VII–B metal component, having an atomic number greater than 25, a Group VIII noble metal component and an alkali-metal component, the latter being preferably potassium and/or lithium. It is particularly preferred that the catalytic composite be substantially free from any "acid-acting" propensities.

The catalytic composite, utilized in the second reaction zone for the primary purpose of effecting the destructive conversion of sulfurous compounds into hydrogen sulfide and hydrocarbons, is a composite of an alumina-containing refractory inorgan oxide, a Group VIII noble metal component and a Group VII–B metallic component, the latter having an atomic number greater than 25.

Through the utilization of a particular sequence of processing steps, under particular conditions of operation and in contact with particular catalytic composites, the formation of high molecular weight polymers and co-polymers is inhibited to a degree which permits processing for an extended period of time. This sequence of processing steps, hereinafter set forth in detail, regulates the overall hydrorefining process in such a manner that the charge stock is never at conditions which foster either coke-forming, or polymerization and co-polymerization reactions during the course fo the process. Briefly, this is accomplished by initiating the hydroefining reactions at temperatures below about 500° F., at which temperatures the coke-forming polymerization reactions are not promoted. As the fresh hydrocarbon charge stock passes through the series of processing steps, its temperature is increased to the necessary level, but only as is consistent with the coke-forming tendencies thereof, as indicated by the reduction in conjugated di-olefins and styrenes.

The operating conditions within the second reaction zone are such that the sulfurous compounds are removed without incurring the detrimental polymerization reactions otherwise resulting were it not for the saturation of the conjugated di-olefinic hydrocarbons in the first reaction zone.

PROCESS CONDITIONS AND OPERATIONS

The process of the present invention is effected in a sequence of contacting zones, each of which is maintained at operating conditions consistent with the chemical characteristics of the hydrocarbon distillate passing therethrough. With some charge stocks, an extreme degree of unsaturation, and high concentrations of contaminating influences, may result in too great a rise in temperature due to the exothermicity of the reaction. In such instances, it may be desirable to provide for multipoint introduction of either the liquid feed, or the recycle hydrogen-rich gas phase, or both, at various intermediate sections of the reaction zone, in order to prevent a high degree of saturation from occurring in one particular portion of the catalyst, and also to provide cooling of the charge stream as it passes through the reaction zone.

The hydrocarbon distillate charge stock, for example a light naphtha by-product from a commercial cracking unit designed and operated for the production of ethylene, having a gravity of about 40.0° API, a bromine number of about 45.7, a diene value of about 35.1 and containing about 400 p.p.m. of sulfur and 73.0 volume percent aromatic hydrocarbons, is admixed with recycled hydrogen. The hydrogen concentration is within the range of from about 500 to about 10,000 standard cubic feet per barrel, and preferably in a narrower range of from about 800 to about 6,000 standard cubic feet per barrel. The charge to the first catalytic reaction zone, heated to a temperature within the range of from about 200° F. to about 500° F., and preferably to a temperature above about 300° F., by way of heat-exchange with various hotter product effluent streams, is introduced into the reaction at a liquid hourly space velocity in the range of from about 0.5 to about 10.0. The reaction zone is maintained at a pressure of from about 100 p.s.i.g. to about 1,000 p.s.i.g., and preferably at a level in the range of from about 500 p.s.i.g. to about 900 p.s.i.g.

The product effluent from the first catalytic reaction zone, preferably without intermediate separation thereof, is introduced into a suitable charge heater wherein the temperature is increased to a level above about 800° F., and preferably in a range of from about 850° F. to about 1000° F. When the process is functioning efficiently, the diene value of the normally liquid hydrocarbonaceous material entering the second catalytic reaction zone is less than about 1.0, and often less than about 0.5. The conversion of nitrogenous and sulfurous compounds and the saturation of mono-olefins, contained within the first zone effluent, is effected in the second catalytic reaction zone, the first zone serving the primary function of selectively saturating the di-olefinic hydrocarbons, without the attendant saturation of aromatic and/or mono-olefinic hydrocarbons, or the removal of sulfur. The second catalytic reaction zone is maintained under an imposed pressure of from about 100 to about 1,000 p.s.i.g., and preferably at a level of from about 500 to about 900 p.s.i.g. However, the process is facilitated when the focal point for pressure control is the second catalytic reaction zone, and, therefore, it will be maintained at a pressure slightly less than the first catalytic reaction zone, as a result of fluid flow through the system. The second catalytic reaction zone has disposed therein a quantity of catalyst sufficient to provide a liquid hourly space velocity therethrough of from about 0.5 to about 10.0, based upon fresh feed. The hydrogen concentration will be in a range of from about 500 to about 10,000 standard cubic feet per barrel, of fresh feed, and preferably from about 1,000 to about 8,000 standard cubic feet per barrel.

The product effluent from the second catalytic reaction zone may be separated in any suitable manner well-known to those possessing expertise in the art, and which method permits recovery of the aromatic-rich naphtha boiling range fraction. Typically, water is added to the product effluent, after it has been cooled to a temperature of from about 60° F. to about 140° F., the mixture being passed into a suitable high-pressure separator equipped with a water dip-leg from which the sour water containing hydrogen sulfide is removed. A hydrogen-rich recycle gaseous phase is withdrawn from the cold separator, and by compressive means, recycled to the first catalytic reaction zone, or the second catalytic reaction zone, or both. Series-flow through the entire system is facilitated when the recycle hydrogen is admixed with the fresh hydrocarbon distillate charge stock. Make-up hydrogen, to supplant that consumed in the overall process may be introduced from any suitable external source, but it is preferably introduced into the system by way of the effluent line from the first catalytic reaction zone.

The gaseous phase from the cold separator may be treated in any suitable manner for the removal of hydrogen sulfide and/or light paraffinic hydrocarbons in order to increase the concentration of hydrogen therein. Similarly, the principally liquid phase from the cold separator may be separated in a hydrogen sulfide-stripping zone, the bottom fraction from which represents the normally liquid product of the process. With respect to the naphtha boiling range portion of the product effluent, the sulfur concentration is less than about 1.0 p.p.m., the aromatic concentration is about 72.2% by volume, the bromine number is less than about 0.5 and the diene value is essentially "nil."

For charge stocks having excessively high diene values, a recycled diluent is employed in order to prevent an excessive temperature rise in the reaction system. Where utilized, the source of the diluent is preferably a portion of the normally liquid effluent emanating from the second catalytic reaction zone. The precise quantity of recycled material varies from feed stock to feed stock; however, the rate is controlled by monitoring the diene value of the combined liquid feed to the first reaction zone. As the diene value exceeds a level of about 25.0, the quantity of recycle is increased, thereby increasing the combined liquid feed ratio; when the diene value approaches a level of 20.0, or less, the quantity of recycled diluent may be lessened, thereby decreasing the combined liquid feed

ratio. Another criteria, employed in controlling the quantity of recycled diluent, is the diene value of the first zone product effluent. It is preferred that this value does not exceed 1.0.

DESCRIPTION OF CATALYTIC COMPOSITES

The catalytic composites utilized in the present process comprise metallic components selected from the metals, and compounds thereof, of Group VII–B, I–A and VIII of the Periodic Table. Thus, in accordance with the Periodic Table of The Elements, E. H. Sargent & Co., 1964, suitable metallic components are selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, technetium, rhenium, ruthenium, rhodium, palladium, osmium, iridium and platinum. It should be noted that the metals selected from Group VII–B, technetium and rhenium, have atomic numbers greater than 25, being 43 and 75 respectively. The use of manganese in the catalyst does not result in the desired degree of hydrogenation selectivity and catalyst stability.

While neither the precise composition, nor the method of manufacturing the catalyst is essential to my invention, certain considerations are preferred. For example, since the charge stocks to the present process are generally naphtha boiling range fractions, and the normally liquid product effluent desired is a naphtha boiling range fraction, it is preferred that neither catalytic composite exhibit an excessive degree of hydrocracking activity, under the operating conditions utilized herein, whereby the naphtha boiling range material is converted into lower-boiling, normally gaseous hydrocarbon products. While an acid-function may be incorporated into the catalytic composite utilized in the second catalytic reaction zone, in order to facilitate the destructive conversion of nitrogenous and sulfurous compounds, the catalytic composite disposed within the first reaction zone is, for the most part, preferably non-acidic. Thus, the catalytically active metallic components are preferably combined with a non-siliceous, substantially halogen-free carrier material such as alumina. A substantially "halogen-free" composite is one wherein halogen is not intentionally added, and, where a halogen compound (chloroplatinic acid) is utilized in the manufacturing process, steps are taken to remove halogen from the composite.

The catalytic composite disposed within the first reaction zone might be said to serve a dual function; that is, it must be non-sensitive to the presence of sulfurous compounds at the operating conditions employed, while at the same time be capable of effecting the partial hydrogenation of conjugated di-olefinic hydrocarbons to the corresponding mono-olefins, while simultaneously possessing a degree of selectivity such that the mono-olefins and aromatic hydrocarbons are not substantially saturated. A catalyst comprising an alumina-containing inorganic oxide, combined with a Group VIII noble metal component, a Group VII–B metal component, having an atomic number greater than 25, and an alkali-metal component, is very efficient in carrying out the desired operation. With respect to the refractory inorganic oxide carrier material, alumina alone, or in combination with minor quantities of the foregoing described inorganic oxides may be advantageously utilized. When two or more refractory inorganic oxides are utilized, for example, alumina and silica, the carrier material has an alumina/silica weight ratio of from about 70/30 to about 90/10. In contrast to the catalytic composite utilized in the second catalytic reaction zone, hereinafter described, it is preferred that the catalyst within the first catalytic reaction zone be substantially free from acid-acting functions, and especially a halogen component. As hereinbefore stated, a halogen compound is often used during one or more steps of the overall manufacturing technique. For example, alumina is commonly prepared by a method which involves digesting aluminum in hydrochloric acid, and a Group VIII noble metal is often impregnated throughout the finished alumina through the use of, for example, chloropalladic or chloroplatinic acid. It is known to be extremely difficult to strip combined halogen from the finished catalyst to a level lower than about 0.1% by weight. The presence of this halogen, which imparts undesired acidity, is countered and inhibited through the use of the alkali-metal component.

The carrier material may be prepared in any suitable manner, and may be either synthetically-prepared or naturally-occurring. Following its preparation, the carrier material may be formed into any desired shape including spheres, pills, cakes, extrudates, powders, granules, etc. Neither the form, nor the method of manufacturing the carrier material is considered to be an essential feature of my invention. One component of the first step catalytic composite is an alkali-metal component employed for the purpose of attenuating the inherent acidity possessed by residual halogen, or by the carrier material. Suitable alkali metals are selected from the group of lithium, sodium, potassium, rubidium, cesium and mixtures thereof, particularly preferred alkali metals being lithium and/or potassium. Regardless of the particular state in which the alkali metal component exists within the final catalytic composite, the quantities thereof, from about 0.05% to about 1.0% by weight, are calculated as if the component existed in the elemental state. It is generally preferred to incorporate the alkali metal component during the preparation of the carrier material; therefore, the carrier material is often referred to as, for example, "lithiated alumina."

At the low temperatures utilized in the first catalytic reaction zone, the Group VIII noble metals possess the propensity for saturating di-olefinic hydrocarbons. The Group VII–B metallic component is combined therewith for the primary purpose of imparting an additional degree of activity such that polymerization and condensation reactions become negligible and hydrogenation of the reactive di-olefins and styrenes is virtually complete, but selectively to mono-olefins and alkyl benzenes.

The Group VIII noble metal component, selected from the group of ruthenium, osmium, rhodium, iridium, palladium, platinum and mixtures thereof, is utilized in an amount of from about 0.01% to about 1.0% by weight, calculated as if existing in the elemental state. The Group VII–B metallic component, selected from technetium and/or rhenium, is also utilized in an amount within the range of from about 0.01% to about 1.0% by weight. Both the Group VIII noble metal component and the Group VII–B metallic component may be incorporated within the catalytic composite in any suitable manner including coprecipitation with the carrier, ion-exchange, or impregnation of the carrier material with a suitable water-soluble compound of the metal. Following the incorporation of the metallic components, for example, by way of impregnation, the carrier material is dried and subjected to a high temperature calcination technique, which technique is well-described within the prior art. A particularly preferred catalytic composite comprises alumina, palladium, lithium and rhenium. Excellent results are achieved with a catalyst containing from about 0.1% to about 0.7% by weight of lithium, 0.3% to about 0.9% by weight of platinum and 0.1% to about 0.8% by weight of rhenium.

While advantageous results are achieved with a catalytic composite having a Group VII–B/noble metal weight ratio in the range of from about 0.05 to 1 to about 2.75 to 1, it is particularly preferred that the catalyst contain an excess of the noble metal component. Exemplary of catalytic composites are those containing: 0.1% by weight of rhenium and 0.65% by weight of platinum; 0.2% by weight of rhenium and 0.5% by weight of palladium; 0.375% by weight of rhenium and 0.375% by weight of platinum; 0.55% by weight of technetium and 0.20% by weight of platinum; 0.65% by weight of rhenium and 0.10% by weight of platinum;

0.10% by weight of technetium and 0.65% by weight of palladium; 0.20% by weight of technetium and 0.55% by weight of platinum; 0.375% by weight of technetium and 0.375% by weight of palladium; 0.375% by weight of rhenium and 0.375% by weight of palladium; 0.55% by weight of technetium and 0.20% by weight of platinum; and, 0.65% by weight of technetium and 0.10% by weight of palladium, etc.

The final catalytic composite will generally be dried at a temperature of from about 200° F. to about 600° F., for a period of from about 2 to about 24 hours. The dry composite is then calcined at a temperature of from about 700° F. to about 1100° F., for a period of about 0.5 to about 10 hours.

With respect to the catalyst composite disposed in the second reaction zone, for the primary purpose of destructively removing sulfurous compounds by the conversion thereof to hydrogen sulfide and hydrocarbons, it must be noted that this reaction zone functions at the significantly higher temperature level of 850° F. to about 1000° F. Therefore, although this catalytic composite is similar to that utilized in the first conversion zone, it is distinctly different therefrom. For example, one component may be a halogen component, the precise form of the association thereof with the carrier material not being accurately known. However, the prior art indicates that it is customary to refere to the halogen component as being combined therewith, or with the other ingredients of the composite, and it is, therefore, commonly referred to as combined halogen. The halogen may be either fluorine, chlorine, iodine, bromine, or mixtures thereof, with fluorine and chlorine being preferred. Bromine and iodine tend to be easily removed from the composite at these operating conditions, and would require at least periodic addition to the reaction zone. The halogen component will be composed in such a manner as results in a final composite containing about 0.1% to about 1.5% by weight, and preferably from about 0.4% to about 0.9% by weight, calculated on an elemental basis. With respect to the alumina-containing carrier material, alumina may be advantageously employed in and of itself, or in combination with minor quantities of silica and/or the previously described refractory inorganic oxides. When combined with, for example, silica, it is preferred that the alumina/silica weight ratio be within the range of from about 63/37 to about 90/10. Suitable carrier materials have physical characteristics indicating an apparent bulk density of about 0.30 to about 0.70 gram per cc., an average pore diameter of from about 20 to 80 angstroms, a pore volume from about 0.1 to about 1.0 millimeter per gram and a surface area of from about 100 to about 500 square meters per gram.

The second-stage catalytic composite also contains a Group VIII noble metal component selected from ruthenium, rhodium, palladium, osmium, iridium and platinum. Of these, a palladium and/or platinum metallic component are especially preferred. This component may exist within the final catalytic composite as a compound, including the oxide, sulfide, halide, etc., or in an elemental state. The Group VIII noble metal component generally comprises about 0.01% to about 1.0% by weight of the final catalytic composite, calculated on the basis of the element. Another constituent of this catalytic composite is a metallic component from Group VII–B, having an atomic number greater than 25, and being either technetium or rhenium. A manganese component is not suitable for use herein since the desired results with respect to the saturation of the mono-olefinic hydrocarbons, and aromatic retention, as well as sulfur tolerability and stability are not obtained. Generally, the rhenium, or technetium component is utilized in an amount sufficient to result in a final catalytic composite containing from about 0.01% to about 1.0% by weight, calculated as the elemental metal. As with the catalytic composite utilized in the first reaction zone, the Group VIII noble metal and Group VII–B metal components may be incorporated within the composite in any suitable manner including co-precipitation, ion-exchange or impregnation. Again, following the incorporation of the metallic components, the carrier material is dried and subjected to a high-temperature calcination technique.

In those instances where the catalytic composite is subjected to a presulfiding operation designed to incorporate from about 0.05% to about 0.50% by weight of sulfur, on an elemental basis, the presulfiding technique is effected upon a reduced composite. That is, prior to the sulfiding technique, the catalytic composite is subjected to substantially water-free reduction in a stream of substantially pure and dry hydrogen containing less than about 30.0 p.p.m., and preferably less than about 5.0 p.p.m. by volume of water.

ILLUSTRATIVE EXAMPLE

This example is presented for the sole purpose of further illustrating the hydrotreating process encompassed by my invention. It is understood that the invention is not to be limited to the particular charge stock, operating conditions, catalytic composites, processing techniques, etc., beyond the scope and spirit of the appended claims. Furthermore, the process will be described with respect to a commercially-scaled unit designed to effect the two-stage catalytic hydrotreating of a mixture of thermally-cracked pyrolysis gasoline. As such, the charge stock, having a gravity of 42.7° API, is a concentrate of pentanes and hydrocarbons boiling up to a temperature of about 375° F. Refinery demands call for a feed pre-fractionation section in which the pyrolysis naphtha is depentanized and rerun to provide a C_6 through C_8 aromatic concentrate. From a total of about 8700 bbl./day of the fresh pyrolysis naphtha, 5000 bbl./day of a C_6 through C_8 fraction (165° F. to about 295° F.) is produced. The characteristics of this aromatic concentrate are: 34.4° API gravity, a bromine number of 40.0, a diene value of about 30.0 and about 200 p.p.m. by weight of sulfur. The aromatic concentration is about 78.6 volume percent.

The rerun column overhead, 5000 bbl./day (690.86 mols/hr.), is combined with 1250 bbl./day (173.12 mols/hr.) of a liquid recycle stream, the source of which is hereafter set forth, and about 1000 s.c.f./bbl. of hydrogen, based upon combined liquid feed. The mixture is raised to a temperature of about 250° F., and enters the first reaction zone at a pressure of about 860 p.s.i.g.

The catalyst in the first reaction zone is a composite of alumina, 0.55% by weight of lithium, 0.375% by weight of palladium and 0.20% by weight of rhenium. The combined feed ratio, 6250/5500 bbl./day is, of course, 1.25, and the liquid hourly space velocity is 3.0, based upon total liquid feed. The product effluent emanates from the reaction zone at a pressure of about 850 p.s.i.g. and a temperature of 310° F. Following suitable heat-exchange, with various hot product effluent streams, to raise the temperature to about 550° F., and the admixture therewith of sufficient hydrogen to increase the concentration to 1500 s.c.f./bbl., the charge is fed to a direct-fired heater wherein the temperature is increased to 850° F. The heated charge is introduced into the second catalytic reaction zone under a pressure of about 800 p.s.i.g.

The second catalytic zone contains a catalyst of a composite of alumina, 0.37% by weight of platinum and 0.20% by weight of rhenium. The catalyst is employed in an amount such that the liquid hourly space velocity is about 3.75. The reaction product effluent is initially passed into a hot separator, at a pressure of about 720 p.s.i.g. and a temperature of about 350° F., following its use as a heat-exchange medium. A principally liquid phase is withdrawn as a bottom stream and utilized in part as the previously mentioned liquid recycle in order to maintain the diene value of the total charge at about 20.0, and provides a combined feed ratio to the first reaction zone of 1.25. The principally vapor phase from the hot separator is introduced, after cooling to a tem-

perature of about 100° F., into a cold separator, from which a hydrogen-rich gaseous phase is removed. The normally liquid stream from the cold separator is combined with that portion of the bottoms stream from the hot separator not used as liquid recycle, the mixture being introduced into a re-boiled stripping column for H_2S removal and depentanization.

In the following Table I, there is presented a component analysis of the total charge to the first reaction zone, the effluent from the first reaction zone and the effluent from the second reaction zone, inclusive of recycled hydrogen and liquid recycle, and prior to separation and recycle of any portion. For convenience, the values are expressed in mols/hr.

TABLE I.—REACTOR EFFLUENT COMPONENT ANALYSES

Component	Total charge	Effluent	
		No. 1	No. 2
Hydrogen sulfide	1.41	1.41	2.68
Hydrogen	690.42	570.62	904.77
Methane	275.75	275.75	459.16
Ethane	43.89	43.89	72.51
Propane	5.87	5.87	9.58
i-Butane	0.42	0.42	0.76
n-Butane	0.52	0.52	0.91
i-Pentane	0.13	0.13	0.30
n-Pentane	0.11	0.11	0.26
C_6–C_8	859.19	859.19	882.90

The ammonia, resulting from the conversion of nitrogenous compounds, is not taken into account in the foregoing table. This is removed by injecting water into the second stage effluent upstream of the cold separator and downstream from the hot separator. Sour water, containing H_2S and the ammonia, is removed from the cold separator by a dip-leg, and transmited to a waste disposal system.

Component analyses of the streams withdrawn from the overall process are presented in the following Table II. These are: the vent gas removed from the H_2S stripper, the vent gas removed from the cold separator, as a result of process presure control, and the bottoms stream from the stripping column. With respect to the stripping column, the top temperature is about 316° F., the top pressure is about 155 p.s.i.g. and the bottoms temperature is about 410° F. At these conditions, the bottoms stream is recovered substantially free from pentanes and lighter hydrocarbons, and can be sent directly to an aromatic recovery system.

TABLE II.—PRODUCT STREAM ANALYSES

Component	Separator vent gas	Stripper vent gas	Stripper liquid product
Hydrogen sulfide	0.51	1.31	----------
Hydrogen	273.42	11.88	----------
Methane	107.99	27.05	----------
Ethane	16.77	15.49	----------
Propane	2.13	5.09	----------
i-Butane	0.14	0.83	----------
n-Butane	0.17	1.21	----------
C_6–C_8	2.19	2.65	686.02

The vent gas stream can be additionally separated by any of the well-known prior art schemes for the purpose of recovering the 4.84 mols/hr. of the C_6–C_8 aromatic concentrate, or any one or more other specific product streams.

With respect to the "as-produced" aromatic concentrate, the sulfur concentration is effectively "nil," the aromatic concentration is 78.1 vol. percent and the diene value is less than about 0.3. The bromine number, indicative of the quantity of mono-olefins, is less than 0.5.

The foregoing specification and example indicate the method by which my invention is effected, and the benefits afforded through the use thereof.

I claim as my invention:

1. A process for hydrorefining an unsaturated, coke-forming hydrocarbon distillate, containing mono-olefinic and di-olefinic hydrocarbons, which process comprises reacting said distillate and hydrogen in a first catalytic reaction zone at a temperature less than about 500° F., in contact with a catalytic composite of an alumina-containing inorganic oxide, a Group VIII noble metal component, a Group VII–B metal component, having an atomic number greater than 25, and added an alkali-metal component, increasing the temperature of the resulting first reaction zone effluent to a level above 800° F., reacting the thus-heated product effluent with hydrogen in a second catalytic reaction, in contact therein with a catalytic composite of an alumina-containing refractory inorganic oxide, a Group VIII noble metal component and a Group VII–B metal component, having an atomic number greater than 25, and separating the resulting second reaction zone effluent to recover said hydrocarbon distillate substantially free from di-olefinic hydrocarbons.

2. The process of claim 1 further characterized in that the hydrocarbon distillate is reacted in said first catalytic reaction zone at a temperature in the range of from about 200° F. to about 500° F.

3. The process of claim 1 further characterized in that said first reaction zone effluent is reacted in said second reaction zone at a temperature of from about 850° F. to about 1000° F.

4. The process of claim 1 further characterized in that a portion of said second reaction zone effluent is recycled to combine with said hydrocarbon distillate in an amount to result in a controlled level of reactive diolefins and styrenes, in the first reaction zone effluent, as indicated by a diene value less than about 1.0.

5. The process of claim 1 further characterized in that said first and second catalytic reaction zones are maintained under an imposed pressure of from about 100 to about 1000 p.s.i.g.

6. The process of claim 1 further characterized in that the catalytic composite disposed in said first catalytic reaction zone comprises alumina, palladium, lithium and rhenium.

7. The process of claim 1 further characterized in that the catalytic composite disposed within said second catalytic reaction zone is a composite of alumina, platinum and rhenium.

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HERBERT LEVINE, Primary Examiner

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