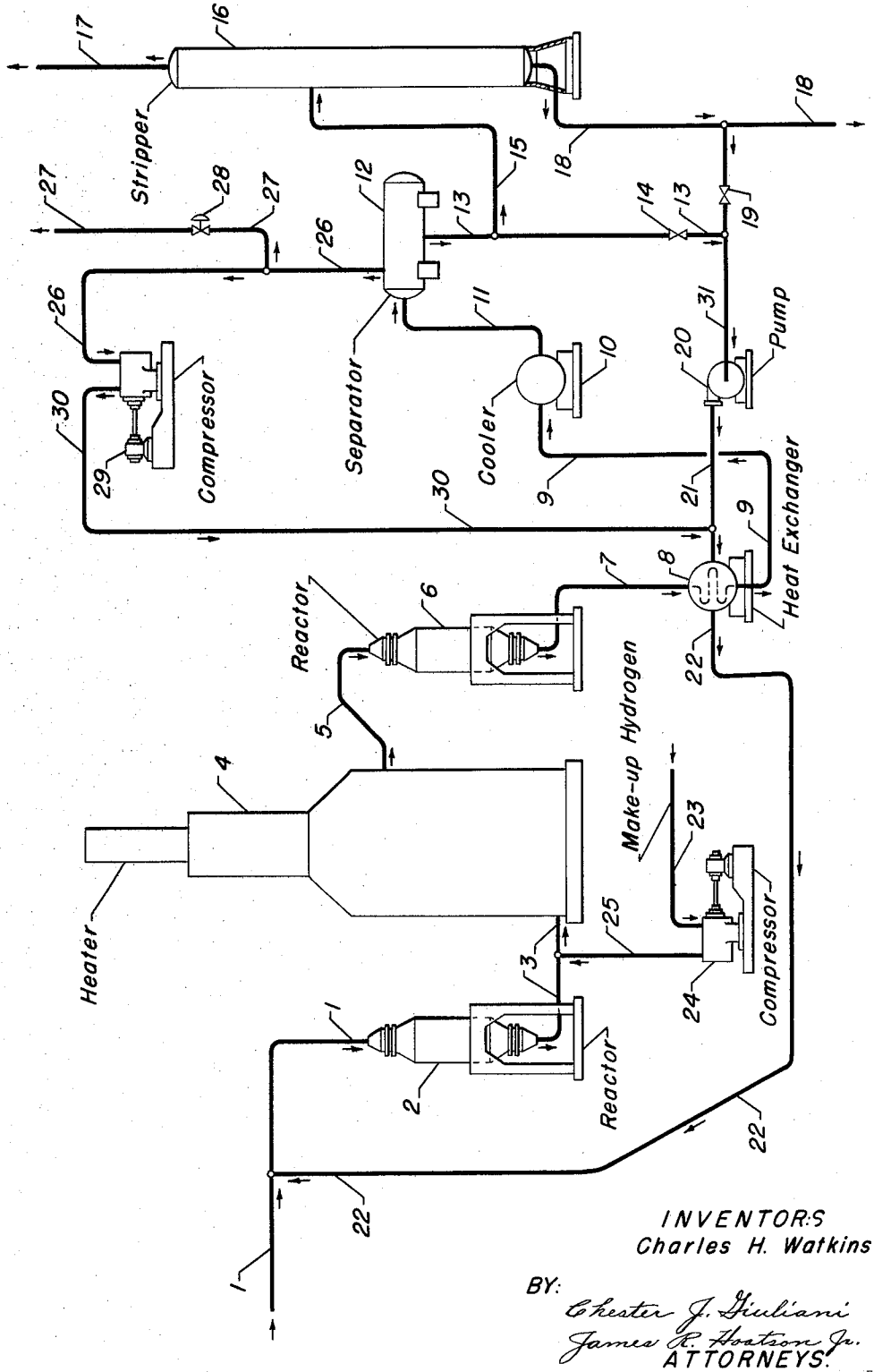
Nov. 2, 1965 C. H. WATKINS 3,215,618

HYDROREFINING OF COKE-FORMING HYDROCARBON DISTILLATES

Filed Sept. 9, 1963



INVENTOR:S
Charles H. Watkins

BY:
Chester J. Giuliani
James R. Hoatson Jr.
ATTORNEYS.

United States Patent Office

3,215,618
Patented Nov. 2, 1965

3,215,618

HYDROREFINING OF COKE-FORMING HYDROCARBON DISTILLATES

Charles H. Watkins, Arlington Heights, Ill., assignor to Universal Oil Products Company, Des Plaines, Ill., a corporation of Delaware

Filed Sept. 9, 1963, Ser. No. 307,746
8 Claims. (Cl. 208—143)

The present application is a continuation-in-part of my copending application, Serial Number 78,961, filed December 28, 1960, now abandoned, which application is incorporated herein by reference. The present invention relates to the hydrorefining of hydrocarbons and mixtures of hydrocarbons, various hydrocarbon fractions and hydrocarbon distillates, for the purpose of removing diverse contaminants therefrom, and/or reacting such hydrocarbons in order to improve the chemical and physical characteristics thereof. More specifically, the process described herein is directed toward the hydrogenation of unsaturated, coke-forming distillate containing mono-olefinic and di-olefinic hydrocarbons, at particular conditions of operation which inhibit the formation of coke and other heavy carbonaceous material otherwise resulting from the hydrorefining of such hydrocarbon fractions and distillates.

In the present specification and appended claims, the terms, "hydrocarbons," "hydrocarbon fractions," "hydrocarbon distillate," and "hydrocarbon mixture," are used interchangeably to connote synonymously various hydrocarbons and mixtures of hydrocarbons resulting from diverse conversion processes. Such conversion processes include catalytic and/or thermal cracking of petroleum, the destructive distillation of wood or coal, shale-oil retorting, etc., and yield various hydrocarbon mixtures which may be advantageously employed as fuels, lubricants and petro-chemical materials, or as charge stocks in processes designed for the production of the same. Such hydrocarbon distillate fractions frequently contain impurities which must necessarily be removed before these distillate fractions are suitable for their intended use, or which, when removed, enhance the value of the distillate fractions for further processing. These impurities include sulfurous compounds, nitrogenous compounds, oxygenated compounds, and various metallic contaminants which cause the hydrocarbon distillate to exhibit corrosive tendencies, and be foul-smelling, thereby making them less desirable for further utilization as a fuel or lubricant, or otherwise.

Probably the most prevalent of the aforementioned impurities is combined sulfur which may exist in the hydrocarbon fraction as mercaptans, thiophenes, sulfide, etc. The combined sulfur is generally removed by the process of hydrodesulfurization, wherein the sulfur-bearing molecule is treated at an elevated temperature above a level of about 500° F., and usually about 700° F. The hydrodesulfurization reaction is effected in the presence of hydrogen and a suitable catalytic composite, the sulfur-bearing molecules being converted to hydrocarbons and hydrogen sulfide, the latter being removed from the process as a gaseous waste material. The same treatment is effective in removing nitrogen-bearing molecules by converting them to the hydrocarbon counterpart and ammonia, the

latter either being removed as a vapor phase, or absorbed from the liquid product effluent. When existing in some combined form, oxygen is less of a removal problem than either sulfur or nitrogen; under the operating conditions employed, oxygenated compounds are readily converted to the hydrocarbon counterpart and water, the latter being removed from the hydrocarbon product by any well-known and suitable means.

However, in addition to the aforementioned contaminants, the hydrocarbon distillates resulting from the various conversion processes hereinbefore set forth contain an appreciable quantity of unsaturated hydrocarbons, both mono-olefinic and diolefinic, the latter including styrene, isoprene, dicyclopentadiene, etc. These unsaturated hydrocarbons induce the coke-forming characteristics of the hydrocarbon distillate, and, when the latter is subjected to hydrodesulfurization for the purpose of removing sulfur, nitrogen and oxygen, there is encountered the difficulty of effecting the desired degree of reaction due to the formation of coke and other carbonaceous material. The deposition of coke and other carbonaceous material appears to be an inherent result of the necessity to effect the hydrodesulfurization process at elevated temperatures, generally in excess of about 500° F. Various heaters, and other appurtenances of the conversion zone experience heavy coking: this appears as formation of solid, highly carbonaceous material resulting from the thermal reaction of the unstable or coke-forming compounds within the hydrocarbon distillate being charged to the unit. In addition, polymerization and copolymerization reactions of the mono-olefins and diolefins are effected within the hydrodesulfurization 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 severe conversion treatments, such as catalytic or thermal cracking or destructive distillation. These distillates are available in a large quantity and generally require the hydrodesulfurization treatment for the purpose of enhancing the possibilities of further usefulness. In many instances, the hydrocarbon distillate will not contain excessive quantities of sulfurous and nitrogenous compounds, but will consist of detrimental amounts of mono-olefins and di-olefins, such that the subsequent use of the hydrocarbon fraction is prohibited. For example, in a thermal cracking process for ethylene production, a full boiling range hydrocarbon product results which 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 about 70.0, and di-olefins in an amount to indicate a diene value of the order of about 30.0 or more. It is the object of the present invention to provide a simple, completely effective method for hydrorefining such coke-forming hydrocarbon distillate fractions without incurring the deposition of extremely large quantities of coke and other carbonaceous material, as well as undesirable gummy polymerization and copolymerization products, onto the catalytic composite, and within the attendant manifolding of the process.

Therefore, in a broad embodiment, the present invention relates to a process for hydrorefining an unsaturated

coke-forming hydrocarbon distillate which comprises reacting said distillate and hydrogen in a first reaction zone, passing the total reaction zone effluent into a second reaction zone, effecting additional reaction of said distillate and added hydrogen, and recycling at least a portion of the effluent from said second reaction zone to combine with said hydrocarbon distillate prior to reacting the same in said first reaction zone.

In another broad embodiment, the present invention provides a process for hydrorefining an unsaturated, coke-forming hydrocarbon distillate containing mono-olefinic and diolefinic hydrocarbons, which comprises reacting said distillate and hydrogen in a first reaction zone, and therein partially hydrogenating said olefinic hydrocarbons, passing the total reaction zone effluent into a second reaction zone, and therein completing the saturation of the olefinic hydrocarbons with additional hydrogen, and recycling at least a portion of the effluent from said second reaction zone to combine with said hydrocarbon distillate prior to reacting the same in said first reaction zone.

In another embodiment, the present invention provides a process for hydrorefining an unsaturated, coke-forming hydrocarbon distillate containing mono-olefinic and di-olefinic hydrocarbons which comprises reacting said hydrocarbon distillate and hydrogen in a first reaction zone at a temperature less than about 500° F. and therein partially hydrogenating said olefinic hydrocarbons, increasing the temperature of the resulting effluent to a level in excess of about 500° F., completing the saturation of the olefinic hydrocarbons with additional hydrogen in a second reaction zone and recycling at least a portion of the effluent from said second reaction zone to combine with said hydrocarbon distillate prior to reacting the same in said first reaction zone.

In a more limited embodiment, the present invention involves a process for hydrorefining an unsaturated coke-forming hydrocarbon distillate containing mono-olefinic and di-olefinic hydrocarbons which comprises reacting said distillate and hydrogen in a first reaction zone containing a hydrorefining catalytic composite of at least one metallic component from the group of metals of Groups VI–A and VIII of the Periodic Table and at a temperature within the range of from about 300° F. to about 500° F. and therein partially hydrogenating said olefinic hydrocarbons, raising the temperature of the resulting effluent to a level of from about 500° F. to about 800° F., completing the saturation of the olefinic hydrocarbons with additional hydrogen in a second reaction zone containing a hydrorefining catalytic composite of at least one metallic component from the group of metals of Groups VI–A and VIII of the Periodic Table, separating the resulting second zone effluent into a gaseous phase and a liquid phase, recombining portions of said gaseous phase and said liquid phase and recycling the resulting mixture to combine with said hydrocarbon distillate prior to reacting the same in said first reaction zone; said liquid phase being recycled in an amount to result in a combined feed ratio to said first reaction zone in excess of about 2:1.

In a more specific embodiment, the present invention relates to a process for hydrorefining an unsaturated, coke-forming hydrocarbon distillate containing mono-olefinic and di-olefinic hydrocarbons which comprises reacting said distillate and hydrogen in a first reaction zone containing a catalytic composite of a non-acidic refractory inorganic oxide, molybdenum and at least one metallic component from the metals of the iron-group of the Periodic Table and at a temperature within the range of from about 300° F. to about 500° F. and therein partially hydrogenating said olefinic hydrocarbons, raising the temperature of the resulting effluent to a level of from about 500° F. to about 800° F., completing the saturation of the olefinic hydrocarbons with additional

hydrogen in a second reaction zone containing a catalytic composite of a non-acidic refractory inorganic oxide, molybdenum and at least one metallic component from the iron-group of the Periodic Table, separating the resulting second reaction zone effluent into a gaseous phase and a liquid phase, recombining portions of said gaseous phase and said liquid phase and recycling the resulting mixture to combine with said hydrocarbon distillate prior to reacting the same in said first reaction zone; said liquid phase being recycled in an amount to result in a combined feed ratio to the first reaction zone of from about 2:1 to about 6:1.

From the foregoing embodiments, it is readily ascertained that the process of the present invention, for the hydrorefining of unsaturated coke-forming hydrocarbon distillates, involves the utilization of two individual, distinctly separated reaction zones. Through the utilization of a particular sequence of processing steps, the formation of high molecular weight polymers and co-polymers, and the yield loss represented by the deposition of coke and other carbonaceous material 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 hydrorefining process such that the charge stock being processed is never at conditions which selectively promote either coke-forming, or polymerization and copolymerization reactions during the course of the process, but which is ultimately hydrorefined at those conditions which would ordinarily produce coke and polymerization products were it not for the particular sequence of processing steps. Briefly, this is accomplished by initiating the hydrorefining at temperatures below about 500° F., and in the presence of a previously hydrorefined, substantially saturated liquid product, at which temperatures the coke-forming polymerization reactions are not promoted selectively. As the fresh hydrocarbon charge stock passes through the series of processing steps, its temperature is increased to the necessary, desired level, but only as is consistent with the coke-forming tendencies thereof.

Furthermore, at an operating temperature less than about 500° F., within the first reaction zone, substantially no desulfurization is effected. In fact, traces of hydrogen sulfide in the hydrogen-rich recycle gas stream react with the olefins to form sulfided hydrocarbons which are then destructively removed in the second reaction zone. The operating conditions within the second reaction zone are such that the sulfurous and nitrogenous compounds are removed without incurring the detrimental polymerization reactions otherwise resulting were it not that saturation of olefins and di-olefins had been effected in the first reaction zone.

In a preferred embodiment, the process of the present invention is effected in a sequence of contacting zones, each of which is maintained at a temperature consistent with the chemical characteristics of the distillate passing therethrough. Another method is to treat the hydrocarbon distillate continuously in a single reaction zone having suitable internal heat exchange equipment, whereby the temperature is adjusted as the charge stock is passed through the catalyst disposed within the reaction zone. In some instances, an extreme degree of unsaturation of the charge stock may result in too great a rise in temperature in the first reaction zone, due to the exothermicity of the reaction; that is, the degree of hydrogenation being effected is indicated by the temperature differential experienced across the reaction zone. In such instances, it may be desirable to provide for multi-point introduction of the charge stock at various intermediate sections of the first 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. On the other hand, internal quench streams may be employed when excessive

temperature rise is an aspect to be considered. Preferably, and particularly in large scale commercial installations, the process of the present invention is most advantageously effected in two or more reaction zones having adequate heat-exchange facilities therebetween.

The process of the present invention may be understood more clearly through reference to the accompanying drawing. It is understood that the drawing, as well as the explanation thereof, is given for the purposes of illustration, and it is not intended to limit the process of the present invention to the particular flow so illustrated. In the interest of simplicity and clarity, various heaters, condensers, valves, controls, instruments, etc., have been eliminated from the drawing; only those vessels and connecting lines necessary for the complete understanding of the process are indicated. In explanation of the drawing, the hydrocarbon charge stock will be assumed identical to that employed in the specific examples hereinafter set forth. This hydrocarbon charge stock is substantially unsaturated, having a bromine number of about 71.7, a diene value of about 27.0, and contains approximately 650 p.p.m. of sulfur. The hydrocarbon charge stock enters the process through line **1**, being admixed therein with a previously hydrorefined product and recycle hydrogen in line **22**, the resulting mixture continuing through line **1** into reactor **2**. The hydrorefined product recycle in line **22**, the source of which is hereinafter described, is employed in an amount to result in a combined feed ratio, to reactor **2**, above about 2:1. The combined feed ratio, is, of course, defined as the ratio of the total liquid hydrocarbon charge to reactor **2**, to the fresh hydrocarbon charge contained therein; preferably, the combined feed ratio will have an upper limit of about 6:1.

An essential feature of the present invention is that the temperature of the material entering reactor **2** be less than about 500° F., having a lower limit of about 300° F., at which temperature substantially no desulfurization takes place, but at least partial hydrogenation of the diolefins and mono-olefins is effected without the attendant polymerization and/or copolymerization thereof. Reactor **2** is maintained under a pressure within the range of from about 500 to about 900 pounds per square inch, which pressure is approximately 20 pounds per square inch higher than that imposed upon reactor **6**, the second stage of the present process, in order to compensate for the normal pressure drop experienced in passing the material to be processed from one reaction zone to the other through the attendant manifolding. The total effluent from reactor **2** is admixed, in line **3**, with make-up hydrogen entering the process through line **23**, being raised to the operating pressure via compressor **24** and passing into line **25**. The resulting mixture passes through line **3** into heater **4** wherein it is heated to a temperature above about 500° F., having an upper limit of about 800° F. The reactor **2** effluent, and added make-up hydrogen, now at an elevated temperature, is passed through line **5** into reactor **6**, the second stage of the present process. Reactor **6** is maintained under an imposed pressure of from about 500 to about 900 pounds per square inch, however, as hereinabove set forth, at a slightly lower pressure than that imposed upon reactor **2**. The elevated temperature in reactor **6** is necessary to complete the saturation of diolefinic and mono-olefinic hydrocarbons, and to convert the remaining nitrogenous and sulfurous compounds into ammonia, hydrogen sulfide and the hydrocarbons. When the process is operating efficiently, the diene value of the liquid hydrocarbons entering reactor **6**, a measure of the concentration of diolefinic hydrocarbons, will be less than about 2.0 and preferably less than about 1.5. The greater degree of conversion of nitrogenous and sulfurous compounds contained within the hydrocarbon charge, is effected in the second reaction zone, the first reaction zone serving the primary function of saturating the diolefins, without the attendant saturation of aromatic hydrocarbons. As hereinafter set forth, the effectiveness of the operation of reactor **2** may be readily ascertained and indicated by the diene value and bromine number exhibited by the final liquid product withdrawn from stripper **16** via line **18**.

The total effluent from reactor **6**, the normally liquid portion of which is substantially completely saturated, is passed via line **7** through heat exchanger **8** and line **9** into cooler **10**. As hereinafter indicated, the function of heat exchanger **8** is to raise the temperature of the recycled hydrorefined product effluent in lines **21** and **22** to a level such that the mixture of fresh hydrocarbon charge and recycled product effluent is at the desired temperature upon entering the reactor **2**. It should be noted that the recycled hydrogen-rich gas stream from compressor **29** passes through line **30** joining the recycled product effluent in line **21**, prior to the mixture being heated in heat exchanger **8**. The temperature of the product effluent from reactor **6** is further lowered in cooler **10**, prior to being passed via line **11** into separator **12**. Separator **12** operates under essentially the identical pressure as reactor **6**, and, in fact, is that point within the process from which the operating pressure imposed on both of the reaction zones is controlled. Separator **12** operates at essentially ambient temperature of the order of about 100° F., or less, and serves to separate the total product effluent from reactor **6** into a gaseous phase and a normally liquid hydrocarbon phase. The gaseous phase, containing hydrogen, ammonia, hydrogen sulfide, and light paraffinic hydrocarbons such as methane, ethane and propane, is withdrawn from separator **12**, via line **26** by compressor **29**, and is passed through line **30** into line **21** wherein it is admixed with at least a portion of the hydrorefined normally liquid hydrocarbons. At least a portion of the gaseous phase is withdrawn from the process through line **27**, containing pressure control valve **28**, for the purpose of preventing a build-up within the system of ammonia and hydrogen sulfide resulting from the conversion of the contaminating sulfurous and nitrogenous compounds. At least a portion of the normally liquid product effluent from reactor **6** is passed from separator **12** via line **13**, containing valve **14**, into line **31**, being raised to the desired operating pressure by pump **20** and passing into heat exchanger **8** via line **21**. As hereinbefore set forth, that quantity of liquid hydrorefined product being recycled by pump **20** is such that the combined feed ratio of the total liquid hydrocarbon material entering reactor **2** lies within the range of from about 2:1 to about 6:1. The excess liquid hydrocarbon from separator **12** is passed via line **15** into stripper **16**. Stripper **16** serves to remove additional ammonia, hydrogen sulfide and light paraffinic hydrocarbons from the system via line **17**. Substantially, completely saturated hydrocarbon products are withdrawn from the process via line **18**.

As indicated in the drawing, the source of the hydrorefined product being recycled to combine with the fresh hydrocarbon charge, may be the stripper bottoms product in line **18**, being withdrawn via line **31** containing valve **19** into pump **20**. Although this particular method has the advantage of recycling only the liquid portion of the hydrorefined product, the particularly preferred method comprises withdrawing such hydrorefined product from separator **12** through line **13** containing valve **14**. This latter scheme has several advantages over the former; the liquid stream from separator **12** is essentially at the operating pressure of reactor **2**, and does not, therefore, require extensive repressuring. Furthermore, the size of the vessel required to serve as stripper **16** is lessened significantly when the recycled hydrorefined product effluent is withdrawn from separator **12**. In some instances, the product stream may be obtained from both sources for the purpose of facilitating the control of the various

temperatures and flow rates within the process. Various modifications may be made to the illustrated embodiment by those possessing skill within the art of petroleum processing, and it is not intended that such modifications shall remove the resulting process from the broad scope and spirit of the appended claims. To illustrate, separator **12** may be combined with additional separating and/or absorbing means, whereby a somewhat different flow pattern and apparatus setup results. For example, water-injection may be provided in line **9**, for the purpose of absorbing the ammonia therein, the water and absorbed ammonia being removed by suitable liquid-level control means from separator **12**. Similarly, the gaseous phase from separator **12** and line **26** may be so treated as to effect substantially complete removal of hydrogen sulfide and/or light paraffinic hydrocarbons. As hereinabove set forth, such modifications are readily recognized by those possessing skill within the art, and are not intended to limit unduly the process of the present invention.

The fresh hydrocarbon charge to reactor **2** will be in an amount to result in a liquid hourly space velocity (defined as volumes of hydrocarbon charge per volume of catalyst disposed within the reaction zone) within the range of from 0.5 to about 10.0. As hereinbefore stated, the quantity of hydrorefined product effluent being recycled in line **22**, to combine with the fresh hydrocarbon charge in line **1**, will be of an amount such that the combined feed ratio to reactor **2** lies within the range of from about 2:1 to about 6:1. The recycled hydrogen-rich gas stream, indicated in the drawing as being admixed with the hydrorefined product effluent in line **21** entering heat exchanger **8**, will be of an amount within the range of from about 500 to about 2500 standard cubic feet per barrel of hydrocarbon charge to the reaction zone. It is preferred, and a more efficient operation is effected when the hydrogen being recycled by compressor **29** through line **30** is less than about 1000 standard cubic feet per barrel of the total hydrocarbon charge entering reactor **2**. Make-up hydrogen may be introduced into the process from any suitable exterior source, and will be of an amount to compensate for the total quantity of hydrogen being consumed within both stages of the process for the destructive removal of sulfurous and nitrogenous compounds, and for the saturation of the diolefinic and monoolefinic hydrocarbons. The make-up hydrogen actually enters the process in the effluent line from the first stage reaction zone: by this method, only the fresh hydrocarbon charge is permitted to pass into the first reaction zone without having been processed in at least one of the two reaction zones.

The two-stage hydrorefining process of the present invention is a catalytic process, and the catalyst employed may be of the same chemical and physical composition in both of the reaction zones. Suitable hydrorefining catalytic composites comprise at least one metallic component selected from the group consisting of the metals of Groups VI–A and VIII of the Periodic Table, and compound thereof. Thus, the catalyst will comprise at least one metallic component selected from the group consisting of chromium, molybdenum, tungsten, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, and mixtures of two or more, etc. The preferred catalytic composite, for utilization in the two-stage process of the present invention, comprises molybdenum and at least one metallic component selected from the iron-group of the Periodic Table. The molybdenum component will generally be in the greater concentration, from about 4.0% to about 30.0% by weight, while the iron-group metallic component will be present in an amount within the range of from about 1.0% to about 6.0% by weight, such concentrations being calculated on the basis of the elemental metal. An essential feature of the catalytic composite is that the catalytically active metallic components, hereinabove set forth, be composited with a non-acidic carrier material. Generally, catalytically active metallic components are composited with any suitable refractory inorganic oxide material including alumina, silica, zirconia, thoria, boria, titania, hafnia, mixtures of two or more, etc. Similarly, other components are often combined with the metallic components and the carrier material; these include the members of the halogen family, particularly fluorine and/or chlorine. However, these components, as well as some of the various refractory inorganic oxides above set forth, impart a particular acid-acting function to the catalytic composite, which function is not desirable in the process of the present invention. For example, a carrier material comprising a combination of alumina and silica, will possess sufficient hydrocracking activity to affect detrimentally the attainment of the specific object of the present invention. Therefore, it is an essential feature of the process of the present invention that the catalytically active metallic components be composited with a non-acidic refractory inorganic oxide carrier material, the term being specifically intended to preclude the utilization of members of the halogen family and other components which might impart an acid-acting function to the catalytic composite. Therefore, a particularly preferred carrier material, for utilization in manufacturing the catalyst employed in the process of the present invention, comprises alumina in its many anhydrous forms, or as aluminum hydroxide. Although any suitable means may be employed for the manufacture of the catalytic composite, a convenient means involves the use of impregnating techniques on a preformed alumina carrier material. For example, a catalyst consisting essentially of about 2.2% by weight of cobalt and about 5.7% by weight of molybdenum, calculated as the elements thereof, may be prepared by impregnating alumina particles of any suitable size and/or shape, with a single impregnating solution of suitable water-soluble compounds, of cobalt and molybdenum. A double impregnation technique may be effected whereby the molybdenum component is first composited, the thus impregnated carrier material being subjected to high-temperature calcination, followed by a second impregnating procedure in which the cobalt component is composited. Suitable water-soluble compounds, for use in preparing the impregnating solution, include molybdic acid, ammonium molybdate, cobalt nitrate hexahydrate, cobalt chloride hexahydrate, nickel nitrate hexahydrate, etc. Following the impregnation, the catalyst is dried at a temperature within the range of from about 200° to about 400° F. and thereafter subjected to a calcination procedure in an atmosphere of air, at an elevated temperature of from about 500° to about 1000° F. Following the calcination of the impregnated carrier material, the composite may be treated in any manner designed to cause the metallic components to exist in a particularly desired form. Thus, the composite may be treated so as to convert the metallic components substantially to the form of oxides, sulfides, sulfates, etc.

When the foregoing conditions of operations and processing techniques are followed, the process encompassed by the present invention is capable of successful, efficient operation for an extended period of time. However, as with virtually all catalytically conducted processes, there exists an inherent, naturally-occurring degree of deactivation of the catalytic composite employed within the reaction zone. Such deactivation is not the rapid deactivation which conceivably could result from various major operating upsets due to interruptions in flow, abrupt changes in operating conditions, etc. In the present two-stage hydrorefining process, the catalyst will ultimately attain a level of deactivation as a result of the natural deterioration of the catalyst during the prolonged period of operation, and the continuing formation of small quantities of coke and other hydrocarbonaceous material. Although the processing techniques of the present invention

permit the utilization of the catalytic composite for an extended period of time, by virtually eliminating the polymerization and copolymerization reactions, it is practically impossible for such elimination to be effected completely. Similarly, the deposition of coke and other carbonaceous material will eventually attain that level at which the catalyst becomes deactivated to the extent that the process is no longer economically feasible. In such instances, the catalyst may be readily reactivated by a rather simple expediency which does not require an extended period of down-time. Following a prolonged period of operation, when it appears that the catalyst has become deactivated to the extent that reactivation is desirable, the introduction of hydrocarbon charge stock is ceased, but the plant pressure is maintained by continuing the circulation of the hydrogen-rich recycle gas stream. For the purpose of regeneration, the temperature of the first-stage of the present process is increased to a level within the range normally maintained upon the second stage of the reaction zone; that is, within the range of from about 500° to about 800° F. The circulating hydrogen-rich gas stream serves to strip the catalyst of the polymerization products formed during the period of operation, and effects such stripping in the relatively short period of from about eight to about twelve hours. In those instances where the catalytic deactivation appears to have resulted from the deposition of coke and carbonaceous material, such material may be effectively removed by burning in an atmosphere of air. The temperature upon the first reaction zone is then decreased to a level below about 500° F., and the fresh hydrocarbon charge, in admixture with hydrorefined recycled product, is reintroduced.

The following examples are given to illustrate further the process of the present invention, and to indicate the benefits afforded through the utilization thereof. It is not intended to limit unduly the process of the present invention to the charge stock, operating conditions, and/or catalytic composite employed within these examples.

EXAMPLE I

The catalyst employed in this example, and in those following, was prepared utilizing 1/8-inch by 1/8-inch cylindrical alumina pills. The alumina pills were impregnated with a single impregnating solution containing sufficient molybdic acid (85% by weight of molybdenum oxide) and cobalt nitrate hexahydrate, to result in a final catalytic composite containing 2.2% by weight of cobalt and 5.7% by weight of molybdenum, calculated as the elements thereof. Following the impregnation of the alumina pills, the composite was dried at a temperature of about 200° F., and calcined at an elevated temperature of about 900° F. in an atmosphere of air. Following the calcination procedure, the temperature was decreased to about 750° F., and the catalyst treated at this temperature with a mixture of hydrogen and hydrogen sulfide for the purpose of converting the cobalt and molybdenum components to the sulfides thereof.

This catalyst was employed in the hydrorefining of a coke-oven light oil, being a hydrocarbon distillate boiling between 176° F. and 322° F., and obtained from the destructive distillation of coal. This charge stock contained 0.382% by weight of sulfur and 22 p.p.m. of nitrogen, both of which existed in some combined form. This charge was processed in a single reaction zone maintained at a temperature 700° F. and under a pressure of about 820 pounds per square inch. Hydrogen was recycled through the catalyst bed at a rate of about 490 standard cubic feet per barrel of hydrocarbon charge. After a few hours of processing at these conditions, the pressure-differential through the reaction zone system became so great that the process had to be shut down. Upon dismantling the reactor section, it was found that the preheater was completely clogged with coke and had to be removed and cleaned before further processing could be effected. When all of the coke and carbonaceous material was removed from the preheater and weighed, it was found that coke had become deposited at a rate of about 6100 pounds of coke per thousand barrels of charge. Stated differently, the coke deposited within the preheater amounted to 2.24% by weight of the total quantity of oil charged to the unit.

The light oil was again treated in the presence of hydrogen and the alumina-cobalt-molybdenum catalyst. However, the processing was effected in two reaction zones rather than the single reaction zone as hereinabove set forth. The charge stock was heated to a temperature of 375° F. and contacted with the catalyst under an imposed pressure of 800 pounds per square inch, and a circulating stream of hydrogen at a rate of 490 cubic feet per barrel. The effluent was removed from the first reaction zone, and immediately heated to 700° F. and again contacted with the catalyst under the same pressure conditions and in the presence of the same circulating hydrogen stream. This operation was continued for several days and yielded a product which contained 0.0018% by weight of sulfur and less than 0.3 p.p.m. of nitrogen. At the end of the run, which was stopped deliberately after a predetermined program, rather than due to processing difficulties, the equipment was dismantled and the preheating element observed as before. The preheater of the low-temperature treating zone contained a deposit which amountd to about 0.19 pound of coke per thousand barrels of charge, a negligible quantity. The preheater of the high-temperature treating zone had no coke deposits therein, and, in fact, had retained its metallic lustre.

EXAMPLE II

A highly olefinic light oil, boiling from about 103° F. to about 340° F., resulting from the steam-cracking of a vacuum gas oil, was contacted with the alumina-cobalt-molybdenum catalyst of the foregoing example at a temperature of 700° F., a pressure of 800 pounds per square inch, and in the presence of a hydrogen stream circulating at the rate of 1000 standard cubic feet per barrel of charge. Clogging of the preheater caused the run to be shut down in a matter of about three hours, and upon dismantling the equipment, it was found that the preheater was clogged with coke, which, when removed and weighed, amounted to about 250 pounds of coke per thousand barrels of charge. The process was again effected, however, employing two stages of processing. The first stage was maintained at a temperature of 420° F. and the second stage at 700° F., with suitable inter-heating between stages, all other conditions being the same as in the initial operation. The process ran for several days with a negligible amount of coke being produced, the unit being shut down deliberately and not as a result of the clogging of the preheater or reactor sections.

EXAMPLE III

The hydrocarbon distillate employed in this and following examples, was a light naphtha by-product from a commercial cracking unit designed and operated for the production of ethylene. Prior to being utilized as fresh hydrocarbon charge stock to the two-stage process of the present invention, this naphtha by-product was rerun for the purpose of removing light paraffinic hydrocarbons and to produce a hydrocarbon distillate having an end boiling point of about 280° F., eliminating those unsaturated hydrocarbons boiling at temperatures above 280° F. As a portion of the by-product of a cracking operation, this hydrocarbon distillate charge stock was characterized by a large proportion of aromatic hydrocarbons, mono-olefinic hydrocarbons, and diolefinic hydrocarbons. Furthermore, the charge was contaminated by the presence of nitrogenous compounds and sulfurous compounds, the latter in an amount of about 650 p.p.m., calculated as elemental sulfur.

The primary object, for which this hydrocarbon distillate charge stock was to be hydrorefined, was to utilize the hydrorefined product effluent as charge material to a unit designed for the recovery of aromatic hydrocarbons such as benzene, toluene, and xylene. Prior to being processed according to the method of the present invention, this particular hydrocarbon charge stock, further characterized by the analyses given in the following Table I, was not suitable as material from which aromatic hydrocarbons were to be recovered; the sulfurous and nitrogenous compounds, as well as the mono-olefins and diolefins, would be recovered in the benzene-concentrate, subsequently interfering with the functions for which such benzene-concentrate was intended. Therefore, it was necessary to effect the destructive removal of the sulfurous and nitrogenous compounds, and to saturate, or hydrogenate, the olefins and diolefins, performing this function in a manner which insured the preservation of aromatic hydrocarbons and the continuous production of a suitable material to be charged to the aromatic recovery system.

Table I

Gravity, °API @ 60° F.	49.8
Specific gravity	0.780
ASTM 100 ml. distillation, ° F.:	
Initial boiling point	126
10%	142
30%	156
50%	173
70%	192
90%	228
End boiling point	279
Sulfur concentration, p.p.m.	650
Bromine number	71.7
Diene value	27.0

This particular portion of the example is given to illustrate the inefficient, unsuccessful operation of the two-stage hydrorefining process when the same is not effected in accordance with the preferred embodiment of the present invention. The various operating conditions and stream inspections prevalent during the operation are given in the following Table II.

passed through the first reaction zone, maintained at an inlet temperature thereto of about 420° F. in the presence of about 2000 M s.c.f./d. of recycle gas, and liquid recycle which was obtained from the first reaction zone effluent, the latter in an amount to yield a combined feed ratio of from about 5.0 to about 6.0. In addition to the fresh hydrocarbon charge, the hydrogen-rich recycle gas, the liquid effluent recycle, the charge to the first reaction zone also contained that quantity of hydrogen required to compensate for that which consumed within the process. The effluent from the first reaction zone was passed into a second reaction zone at an inlet temperature thereto of about 600° F. In this type of operation, several various items may be employed to indicate the effectiveness of the operation: the pressure differential, measured from the discharge of the recycle gas compressor to the controlled pressure of the high-pressure separator in the effluent line from the second reaction zone, is indicative of that quantity of polymerization products which have been deposited within the reaction zone and the attendant piping; the temperature differential across each of the two catalyst beds is an indication of the degree of saturation being effected within the particular reaction zone. In addition, the quantity of unsaturated hydrocarbons contained within the stripper bottoms fraction, as measured by the bromine number and diene value thereof, indicates the over-all efficiency of the process, since, for all practical purposes, these figures should be nil.

As indicated in Table II, the unit was operated for a period of 12 consecutive days, being shut down on the 13th day of operation as a result of the pressure differential having increased to a level of about 100 pounds per square inch. Shortly beore the unit was shut down, the various diene values on the several streams were determined as follows: the reactor charge had a diene value of 29.3; the diene value of the recycled liquid stream, from the effluent of the first reaction zone to the inlet of the first reaction zone, was 1.7; the stripper bottoms fraction indicated a diene value of 0.15 and this stream was indicated as being sour by the "doctor" test. Upon inspection of the catalyst in the first reaction zone, a gummy residue was discovered to be extending approximately

Table II

Days on Stream	1	3	6	8	11	12
Operating Conditions:						
Reactor #1 Inlet Temp., ° F	419	419	420	416	422	423
Reactor #1 Differential, ° F	27	33	35	34	31	35
Reactor #2 Inlet Temp., ° F	587	587	594	592	600	601
Reactor #2 Differential, ° F	114	110	107	107	118	114
Compressor Discharge Pressure, p.s.i	780	785	790	800	820	833
Separator Pressure, p.s.i	750	750	750	750	750	750
Pressure Differential, p.s.i	30	35	40	50	70	83
Charge Rates:						
Reactor #1 Charge, b./d	825	975	955	845	946	953
Recycle to Reactor #1, b./d	5,760	4,350	4,130	4,040	4,250	4,250
Recycle Gas to Reactor #1, M s.c.f./d	2,150	2,080	2,050	2,080	1,855	1,940
Combined Feed Ratio	8.0	5.5	5.3	5.8	5.5	5.4
Stream Inspections:						
Reactor #1 Charge:						
Specific Gravity	.785	.785	.785	.785	.787	.796
I.B.P., ° F	106	100	108	100	104	102
50%, ° F	165	169	166	164	162	174
E.P., ° F	275	269	273	264	236	256
Diene Value				29.8		
Recycle to Reactor #1:						
Diene Value	1.7	1.7	1.1	1.5		
Bromine Number	56.2	62.0				
Stripper Bottoms:						
Specific Gravity	.838	.831			.842	.837
I.B.P., ° F	170	170	170	174	174	168
50%, ° F	202	200	200	200	198	200
E.P., ° F	436	410		380	426	411
Diene Value						
Bromine Number	0.18	0.18	0.28	0.22		

The catalytic composite, disposed in both of the reaction zones, was a pre-sulfided composite of alumina, 2.2% by weight of cobalt and 5.7% by weight of molybdenum, calculated as the elements thereof. The charge stock

⅓ of the way into the catalyst bed. The catalyst was regenerated with air to remove coke and hydrocarbonaceous material, and pre-sulfided with hydrogen sulfide at a temperature of about 715° F. Following the regeneration

of the catalyst in the first reaction zone, the unit was operated for a period of 14 days, the first ten of which are indicated in the following Table III.

Table III

Days on Stream	1	3	6	9	10
Operating Conditions:					
Reactor #1 Inlet Temp., ° F.	420	428	430	429	432
Reactor #1 Differential, ° F.	30	36	34	39	32
Reactor #2 Inlet Temp., ° F.	593	596	598	603	578
Reactor #2 Differential, ° F.	123	124	126	132	168
Compressor Discharge Pressure, p.s.i.	770	770	775	780	795
Separator Pressure, p.s.i.	750	750	750	750	750
Pressure Differential, p.s.i.	20	20	25	30	45
Charge Rates:					
Reactor #1 Charge, b./d.	933	976	840	1,000	1,230
Recycle to Reactor #1, b./d.	4,675	4,250	4,250	3,700	5,300
Recycle to Gas to Reactor #1, M s.c.f./d.	2,250	2,120	2,000	2,000	2,050
Combined Feed Ratio	5.9	5.4	6.0	4.7	5.3
Stream Inspections:					
Reactor #1 Charge:					
Specific Gravity	.782	.777	.774	.775	.770
I.B.P., ° F.	98	107	104	104	108
50%, ° F.	164	161	162	160	158
E.P., ° F.	274	272	272	280	250
Diene Value	------	27.2	------	------	27.2
Recycle to Reactor #1:					
Diene Value	2.0	1.8	------	1.7	3.6
Bromine Number	66.4	61.0	27.5	34.2	33.8
Stripper Bottoms:					
Specific Gravity	.825	.820	------	.810	------
I.B.P., ° F.	152	158	------	162	------
50%, ° F.	190	192	------	192	------
E.P., ° F.	428	424	------	------	------
Diene Value	0.69	0.54	------	------	0.15
Bromine Number	------	0.30	------	0.32	------

On the fourteenth day of this operation, the unit was shut down due to a pressure differential of 80 pounds per square inch. Upon inspection of the first stage reactor system, it was found that the charge lines leading to the reactor vessel were extremely clogged with coke and other carbonaceous material, and, just prior to the bed of catalyst, a gummy polymerization product was found. As indicated in Table III, even the first ten days of this operation were unsatisfactory: the diene value of the first stage effluent had increased to 3.6, the first stage apparently saturating selectively the mono-olefins (as evidenced by the decrease in the Bromine Number); the stripper bottoms (ultimate charge to the aromatic recovery unit) indicated a diene value from 0.15 to about 0.5, and was further contaminated by mono-olefins; furthermore, the second-stage temperature differential increased from about 130° F. to about 170° F., indicating that this second stage was being forced to perform functions designed to be effected in the first stage. The catalyst in the first stage was regenerated as before, being sulfided in situ with hydrogen sulfide at a temperature of 715° F. The next operation was in progress for only ten days, the pressure differential again increasing to a level of 80 pounds per square inch, with the diene value of the first-stage effluent increasing to 2.85.

During the next few operating periods, the make-up hydrogen was introduced into the second-stage reaction zone, the only hydrogen passing into the first stage being that which was recycled from the high-pressure separator. The pressure differential, in twelve operating days, increased only 5.0 pounds per square inch, but the diene value on the reaction zone effluent increased to 2.73, while the bromine number on the stripper bottoms fraction increased from 0.18 to 0.43, this stream turning "doctor" sour.

The next two operations, of nine and five days duration, indicated results similar to those previously experienced; in the first, the diene value of the first-stage effluent increased to 4.98 and the bromine number of the stripper bottoms to 1.43; the last five-day operation was terminated when the diene value became 5.23, and the bromine number 1.5. In both operations, the pressure differential increased steadily, approximately 5.0 pounds per square inch per day.

The unit was again shut down and inspected for coke and carbonaceous deposits and polymerization products. Changes in the process flow were made such that the unit conformed to the preferred flow of the present invention: provisions were made to obtain the liquid recycle material from the second stage liquid effluent stream at the high pressure separator, and to control the temperature thereof via heat exchange with the total second stage effluent; it was decided to continue introducing the make-up hydrogen into the second stage reaction zone, since this scheme had previously exhibited an apparent beneficial effect in maintaining a pressure differential from the recycle compressor discharge to the high-pressure receiver. As a result of these changes, the liquid charge to the first stage reaction zone would be substantially diluted with a virtually completely saturated, previously hydrorefined product, whereby the degree of unsaturation of the total charge would be lessened considerably, and there would be less of an opportunity for oxygen to enter the first-stage reaction zone, since the only gaseous material being introduced thereto would have already been subjected to processing in both reaction zones.

The operating conditions and stream inspections are given in the following Table IV:

Table IV

Days on Stream	1	2	3	4	5	6	7
Operating Conditions:							
Reactor #1 Inlet Temp., ° F.	411	410	409	413	412	412	412
Reactor #1 Differential, ° F.	75	82	70	62	48	64	66
Reactor #2 Inlet Temp., ° F.	682	682	672	674	674	674	674
Reactor #2 Differential, ° F.	35	45	50	45	44	32	38
Reactor #1 Pressure, p.s.i.	------	------	------	------	------	------	765
Reactor #2 Pressure, p.s.i.	------	------	------	------	------	------	745
*Plant Pressure Differential, p.s.i.	27	27	30	30	30	30	30
Charge Rates:							
Reactor #1 Charge, b./d.	584	564	532	486	560	430	496
Recycle to Reactor #1, b./d.	1,155	1,155	1,155	1,155	1,155	1,120	1,120
Recycle Gas to #1 Reactor, M s.c.f./d.	3,500	3,500	3,500	3,500	3,500	3,500	3,300
Combined Feed Ratio	3.0	3.1	3.2	3.4	3.1	3.6	3.3
Stream Inspections:							
Reactor #1 Charge:							
Specific Gravity	.795	8.05	.788	.787	------	------	.776
I.B.P., ° F.	98	98	96	103	------	------	103
50%, ° F.	194	192	180	185	------	------	175
E.P., ° F.	282	284	283	282	------	------	271
Diene Value	------	------	------	------	------	------	------
Reactor #1 Effluent: Diene Value	------	------	0.23	------	------	------	------
Stripper Bottoms:							
Specific Gravity	.808	.826	.830	.821	.821	------	.804
I.B.P., ° F.	156	166	160	158	160	------	158
50%, ° F.	186	214	208	203	206	------	192
E.P., ° F.	418	400	410	406	------	------	360
Bromine Number	0.22	0.23	0.24	0.22	------	------	0.18
Diene Value	0.17	------	------	------	------	------	------

Days on Stream	8	9	10	11	12	13	14
Operating Conditions:							
Reactor #1 Inlet Temp., ° F	412	414	414	412	416	415	414
Reactor #1 Differential, ° F	62	81	77	76	67	69	65
Reactor #2 Inlet Temp., ° F	678	678	676	676	672	670	667
Reactor #2 Differential, ° F	42	45	48	49	57	59	57
Reactor #1 Pressure, p.s.i	765	765	765	765	768	768	768
Reactor #2 Pressure, p.s.i	745	743	745	742	740	745	745
*Plant Pressure Differential, p.s.i	28	32	33	35	35	36	37
Charge Rates:							
Reactor #1 Charge, b./d	512	545	627	560	671	665	584
Recycle to Reactor #1, b./d	1,120	1,120	1,155	1,250	1,250	1,250	1,250
Recycle Gas to #1 Reactor, M s.c.f./d	3,300	3,300	3,300	3,300	3,300	3,300	3,300
Combined Feed Ratio	3.2	3.1	2.8	3.2	2.9	2.9	3.1
Stream Inspections:							
Reactor #1 Charge:							
Specific Gravity	.775	.770	.765	.766	.774	.767	.765
I.B.P., ° F	98	98	100	98	100	101	101
50%, ° F	162	166	163	160	162	170	166
E.P., ° F	269	274	271	262	279	276	270
Diene Value							
Reactor #1 Effluent: Diene Value				0.235			
Stripper Bottoms:							
Specific Gravity	.810	.804	.802		.802	.803	.801
I.B.P., ° F	142	151	158		155	156	158
50%, ° F	194	191	193		197	197	192
E.P., ° F	387	363	396		359	393	398
Bromine Number	0.16		0.19		0.31	0.16	0.18
Diene Value							

Days on Stream	15	16	17	18	19	20	21
Operating Conditions:							
Reactor #1 Inlet Temp., ° F	415	411	410	412	410	410	412
Reactor #1 Differential, ° F	67	76	82	88	86	88	67
Reactor #2 Inlet Temp., ° F	664	663	663	663	663	662	660
Reactor #2 Differential, ° F	62	67	62	67	68	69	70
Reactor #1 Pressure, p.s.i	765	768	765	765	765	765	765
Reactor #2 Pressure, p.s.i	745	745	745	745	745	745	740
*Plant Pressure Differential, p.s.i	37	35	37	35	35	35	37
Charge Rates:							
Reactor #1 Charge, b./d	550	541	558	540	555	530	526
Recycle to Reactor #1, b./d	1,250	1,250	1,250	1,250	1,250	1,250	1,250
Recycle Gas to #1 Reactor, M s.c.f./d	3,300	3,300	3,300	3,300	3,300	3,300	3,300
Combined Feed Ratio	3.3	3.3	3.2	3.3	3.3	3.4	3.4
Stream Inspections:							
Reactor #1 Charge:							
Specific Gravity	.767	.766	.764	.765	.763		.772
I.B.P., ° F	114	104	98	106	99		98
50%, ° F	158	160	160	156	162		182
E.P., ° F	268	270	270	265	272		292
Diene Value				24.6			
Reactor #1 Effluent: Diene Value		0.25					
Stripper Bottoms:							
Specific Gravity	.799	.798	.803	.797	.798	.797	
I.B.P., ° F	156	158	156	156	157	156	
50%, ° F	192	190	190	191	190	190	
E.P., ° F	380	378	376	377	344	340	
Bromine Number	0.31	0.44	0.24	0.19	0.23	0.19	
Diene Value							

Days on Stream	22	23	24	25	26	27
Operating Conditions:						
Reactor #1 Inlet Temp., °F	414	410	412	410	413	412
Reactor #1 Differential, °F	67	60	55	60	58	62
Reactor #2 Inlet Temp., °F	663	655	656	656	656	654
Reactor #2 Differential, °F	72	73	72	73	75	75
Reactor #1 Pressure, p.s.i	765	770	770	770	770	770
Reactor #2 Pressure, p.s.i	740	740	742	747	740	740
*Plant Pressure Differential, p.s.i	35	35	37	38	39	39
Charge Rates:						
Reactor #1 Charge, b./d	529	614	607	615	545	505
Recycle to Reactor #1, b./d	1,250	1,250	1,250	1,250	1,250	1,250
Recycle Gas to Reactor #1, M s.c.f./d	3,300	3,300	3,300	3,300	3,300	3,300
Combined Feed Ratio	3.4	3.0	3.1	3.0	3.3	3.5
Stream Inspections:						
Reactor #1 Charge:						
Specific Gravity	.773	.773	.770	.766	.767	.766
I.B.P., ° F	101	93	97	92	90	94
50%, ° F	182	180	184	164	169	170
E.P., ° F	289	289	296	284	201	273
Diene Value				16.8		
Reactor #1 Effluent: Diene Value		0.18				
Stripper Bottoms:						
Specific Gravity	.803	.799	.802	.801	.799	.802
I.B.P., ° F	159	158	156	158	156	166
50%, °F	210	209	208	207	202	200
E.P., ° F	368	384	326	382	394	409
Bromine Number	0.24	0.19	0.22	0.22	0.31	
Diene Value						

*Pressure Differential from Compressor Discharge to High-Pressure Separator.

It is immediately ascertained that the method of the present invention effected a significant change in the operation of the unit. After 27 days of operation, almost three times the duration of the majority of the previous runs, the pressure differential had increased only twelve pounds per square inch, or less than about 0.5 pound per

operating day. The diene value of the first-stage effluent was consistently less than 0.3, that of the stripper bottoms fraction (after the first day of operation) being nil, the latter stream also being continuously "doctor" sweet. Of further significance is the fact that the combined feed ratio was lowered to about 3.5; this result will permit ultimately increasing the quantity of fresh charge to the unit since the reaction zone is designed considering the total quantity of hydrocarbons to be introduced thereto.

The foregoing specification and examples, particularly the last example and the data shown in Table IV, indicate clearly the method of the present invention and the benefits to be afforded the two-stage hydro-refining process through the utilization 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 comprises reacting said hydrocarbon distillate and hydrogen in a first reaction zone at a temperature less than about 500° F. and therein partially hydrogenating said olefinic hydrocarbons, increasing the temperature of the resulting effluent to a level in excess of about 500° F., completing the saturation of the olefinic hydrocarbons with additional hydrogen in a second reaction zone and recycling at least a portion of the effluent from said second reaction zone to combine with said hydrocarbon distillate prior to reacting the same in said first reaction zone.

2. The process of claim 1 further characterized in that said hydrocarbon fraction is reacted in said first zone at a temperature of at least about 300° F., and the temperature of the resulting first reaction zone effluent is increased to a level within the range of from about 500° F. to about 800° F.

3. The process of claim 1 further characterized in that said second reaction zone effluent is recycled to combine with said hydrocarbon fraction in an amount to result in a combined feed ratio in excess of about 2:1.

4. A process for hydrorefining an unsaturated coke-forming hydrocarbon distillate containing mono-olefinic and di-olefinic hydrocarbons which comprises reacting said distillate and hydrogen in a first reaction zone containing a hydrorefining catalytic composite of at least one metallic component from the group of metals of Groups VI–A and VIII of the Periodic Table and at a temperature of at least about 300° F. but below about 500° F. and therein partially hydrogenating said olefinic hydrocarbons, raising the temperature of the resulting effluent to a level of from about 500° F. to about 800° F., completing the saturation of the olefinic hydrocarbons with additional hydrogen in a second reaction zone containing a hydrorefining catalytic composite of at least one metallic component from the group of metals of Groups VI–A and VIII of the Periodic Table, separating the resulting second zone effluent into a gaseous phase and a liquid phase, recombining portions of said gaseous phase and said liquid phase and recycling the resulting mixture to combine with said hydrocarbon distillate prior to reacting the same in said first reaction zone; said liquid phase being recycled in an amount to result in a combined feed ratio to said first reaction zone in excess of about 2:1.

5. The process of claim 4 further characterized in that said combined feed ratio is within the range of from about 2:1 to about 6:1.

6. The process of claim 4 further characterized in that the hydrorefining catalyst disposed in said first and second reaction zones comprises molybdenum and at least one metallic component from the metals of the iron-group of the Periodic Table.

7. A process for hydrorefining an unsaturated, coke-forming hydrocarbon distillate containing mono-olefinic and di-olefinic hydrocarbons which comprises reacting said distillate and hydrogen in a first reaction zone containing a catalytic composite of a non-acidic refractory inorganic oxide, molybdenum and at least one metallic component from the metals of the iron-group of the Periodic Table and at a temperature of at least about 300° F. but below about 500° F. and therein partially hydrogenating said olefinic hydrocarbons, raising the temperature of the resulting effluent to a level of from about 500° F. to about 800° F., completing the saturation of the olefinic hydrocarbons with additional hydrogen in a second reaction zone containing a catalytic composite of a non-acidic refractory inorganic oxide, molybdenum and at least one metallic component from the iron-group of the Periodic Table, separating the resulting second reaction zone effluent into a gaseous phase and a liquid phase, recombining portions of said gaseous phase and said liquid phase and recycling the resulting mixture to combine with said hydrocarbon distillate prior to reacting the same in said first reaction zone; said liquid phase being recycled in an amount to result in a combined feed ratio to the first reaction zone of from about 2:1 to about 6:1.

8. The process of claim 7 further characterized in that the catalytic composite in said first and second reaction zones comprises alumina, from about 4.0% to about 30.0% by weight of molybdenum and from about 1.0% to about 6.0% by weight of at least one metallic component from the metals of the iron-group of the Periodic Table, calculated as the elements thereof.

References Cited by the Examiner

UNITED STATES PATENTS

2,303,075	11/42	Frey	260—683.9
2,303,118	11/42	Frey	260—683.9
2,332,572	10/43	Hepp et al.	260—683.9
2,878,179	3/59	Hennig	208—144
2,889,264	6/59	Spurlock	208—143
2,901,417	8/59	Cook et al.	208—210
2,906,784	9/59	Dean et al.	208—144
2,983,676	5/61	Howland	208—218
2,990,431	6/61	Cabbage	260—667

ALPHONSO D. SULLIVAN, *Primary Examiner.*