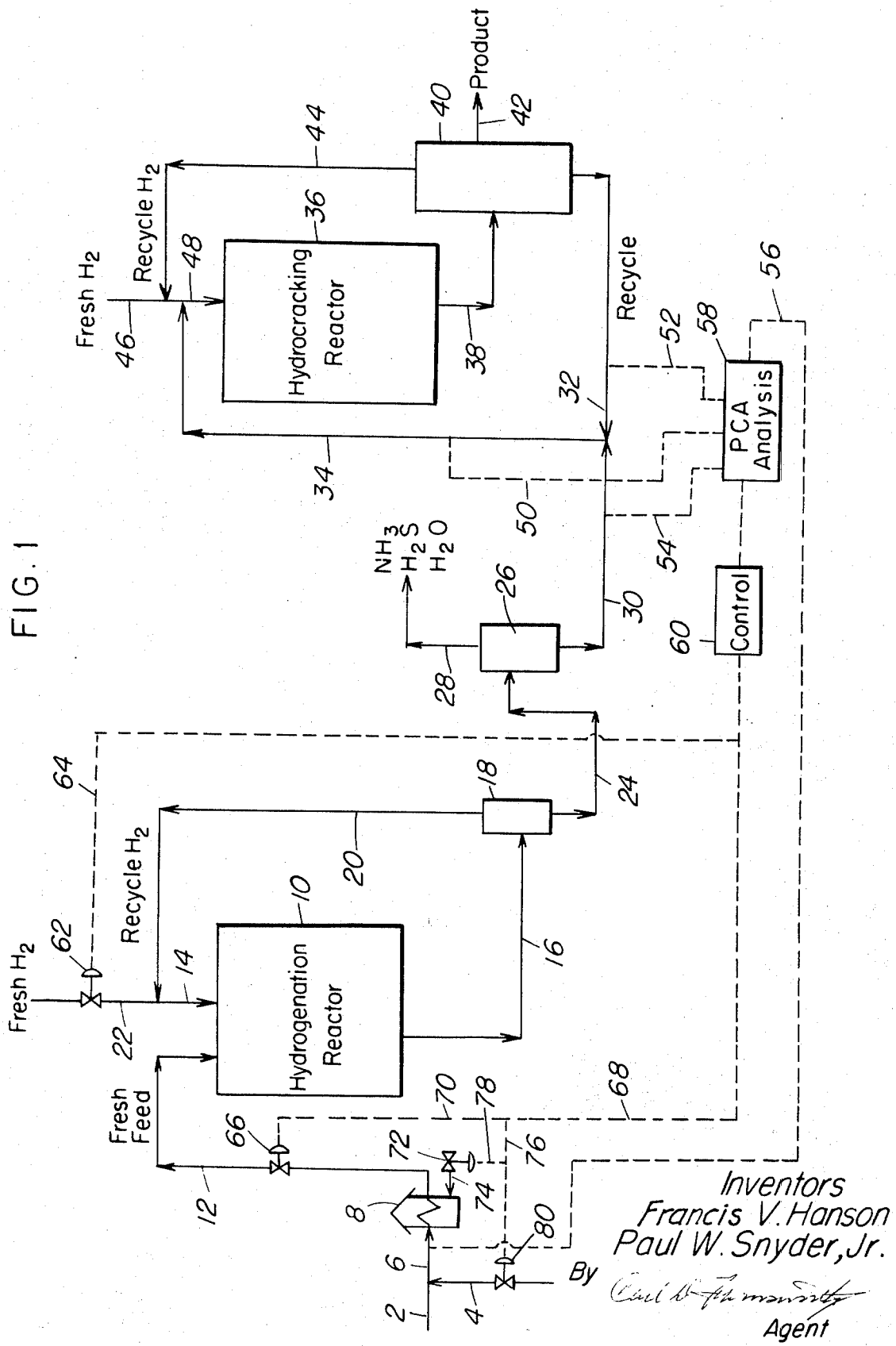
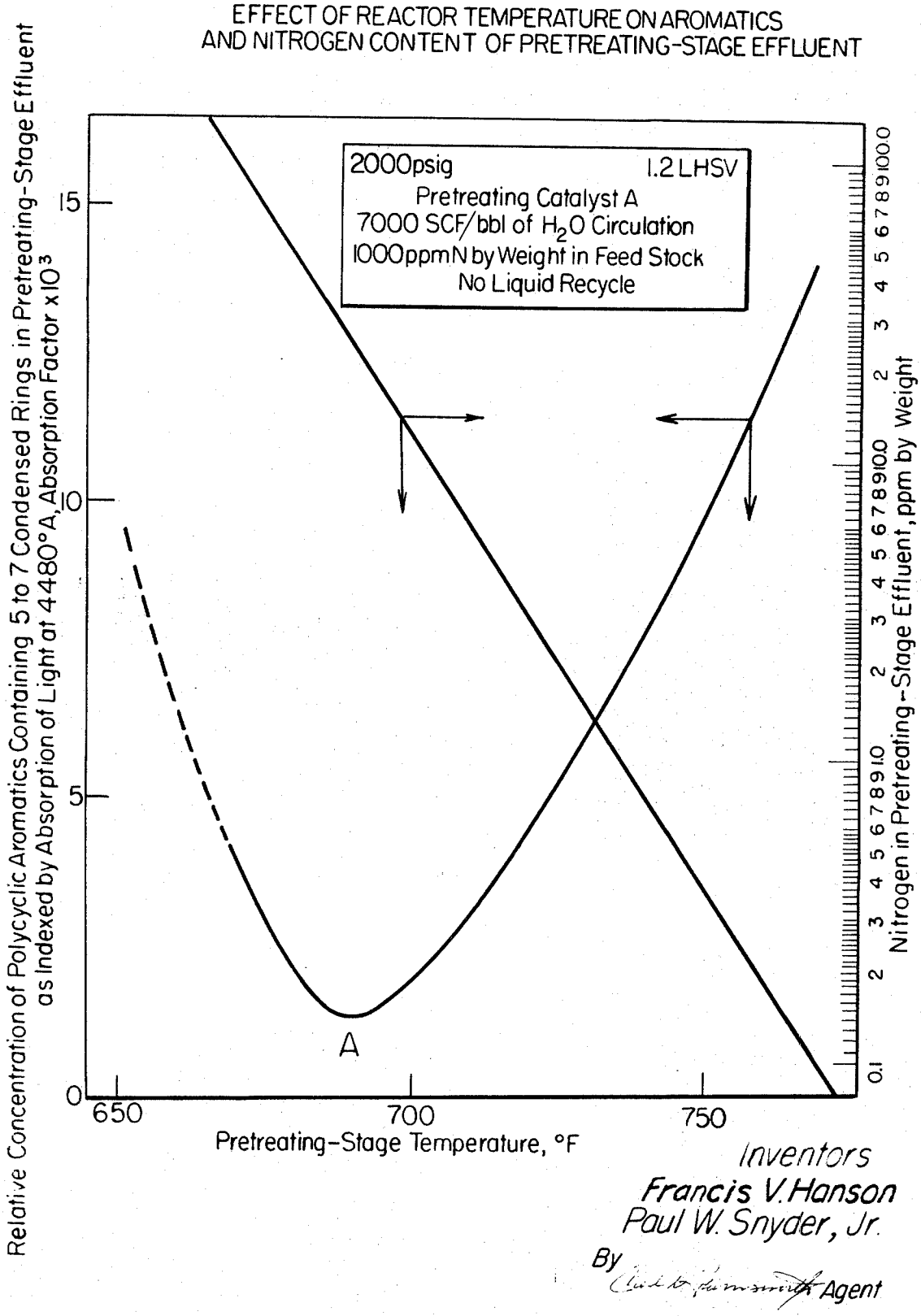
Aug. 15, 1972 F. V. HANSON ET AL 3,684,694
METHOD OF CONTROLLING INTERACTION BETWEEN PRETREATING AND HYDROCRACKING STAGES
Original Filed March 6, 1968 3 Sheets-Sheet 1

FIG. 1



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FIG. 2



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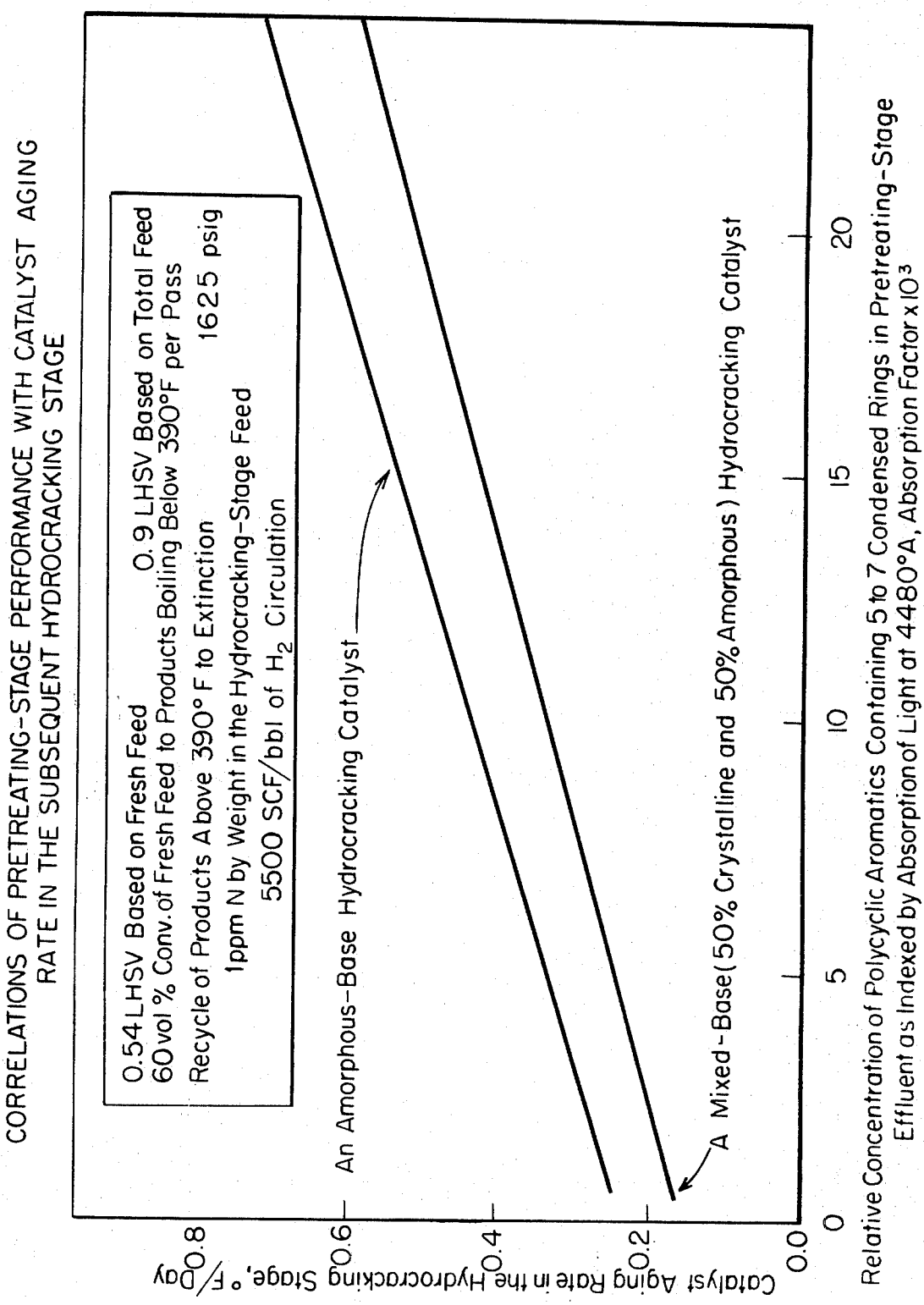


FIG. 3

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United States Patent Office 3,684,694
Patented Aug. 15, 1972

3,684,694

METHOD OF CONTROLLING INTERACTION BETWEEN PRETREATING AND HYDROCRACKING STAGES

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Continuation of application Ser. No. 710,901, Mar. 6, 1968. This application May 26, 1970, Ser. No. 41,702
Int. Cl. C10g 23/00
U.S. Cl. 208—89 5 Claims

ABSTRACT OF THE DISCLOSURE

A method of determining and controlling the concentration of polycyclic aromatic compounds in various hydrocarbon streams of a multi-stage process comprising pretreating and hydrocracking is described. The method comprises employing ultraviolet and visible light to determine the concentration of three or more condensed-ring polycyclic aromatics in hydrocarbon streams and in response to the measured concentration of condensed-ring polycyclic aromatics, control means are operated to vary the raw feed composition to the process comprising feed pretreat followed by hydrocracking thereof, the conditions employed in the pretreat stage so as to control the concentration of polycyclic aromatics in the effluent therefrom and the concentration of polycyclic aromatics in the hydrocarbon charge to the hydrocracking stage of the process particularly when recycle produce of the hydrocracking step is returned thereto.

This application is a continuation of Ser. No. 710,901 filed Mar. 6, 1968, now abandoned.

BACKGROUND OF THE INVENTION

Recently, there has been increased incentive to use hydrocracking processes to produce fuel products and especially gasoline products. Hydrocracking is useful in converting relatively refractory feeds containing high boiling polycyclic aromatic hydrocarbons or other high boiling hydrocarbons to lower boiling products such as gasoline without excessive gas or coke formation. These same refractory feeds however when charged to a catalytic cracking process operated in the substantial absence of hydrogen gas, effect excessive coke formation on the catalyst, and thus seriously reduce the catalyst activity and its ability to maintain product yield. Present hydrocracking processes generally include at least two zones or stages of catalytic treatment comprising a first hydrocarbon feed pretreating-hydrogenation stage followed by one or more stages of hydrocracking.

The pretreating stage is employed to at least effect a reduction in sulfur and nitrogen concentrations in the feed by converting compounds of these elements to hydrogen sulfide and ammonia, respectively. It has been found that nitrogen compounds usually found in hydrocracking feeds adversely reduce the cracking activity of most hydrocracking catalysts and often accelerate catalyst deactivation when present. When this occurs, frequent regenerations become necessary to maintain a desired hydrocarbon conversion rate by hydrocracking. The deleterious effects of nitrogen, sulfur and carbonaceous residue are particularly evident when an amorphous or non-crystalline base hydrocracking catalyst is employed in the hydrocracking stages. Hydrocracking catalysts comprising a crystalline aluminosilicate are less adversely affected by nitrogen and sulfur concentrations in the feed than are the amorphous base hydrocracking catalysts; however, many sources of petroleum hydrocracking feeds contain high concentrations of organic nitrogen compounds and in amounts which seriously adversely affect the activity of these catalysts. Thus, the hydrocarbon feed to be passed in contact with a crystalline aluminosilicate containing hydrocracking catalyst also often requires a preliminary pretreating or hydrogenation step to reduce the sulfur and nitrogen concentrations of the feed to desired low levels so as to achieve optimum hydrocracking catalyst performance.

A crystalline aluminosilicate containing hydrocracking catalyst generally exhibits increased cracking activity for relatively large portions of the feed, and an improved selectivity as compared to the amorphous-base catalyst. It is these characteristics of the crystalline aluminosilicate containing hydrocracking catalysts which have promoted their increased use in hydrocracking processes. However, the crystalline aluminosilicate containing hydrocracking catalysts suffer the disadvantage of exhibiting a poor ability for cracking relatively high molecular weight polycyclic hydrocarbons as compared to the amorphous-base hydrocracking catalyst. This is probably due to intraparticle diffusion limitations caused by the relatively small pore sizes of the crystalline aluminosilicate. Thus, when employing a crystalline aluminosilicate containing hydrocracking catalyst, having a pore size in the range of 6 to 15 angstroms, and when recycling at least a portion of the heavier products of single-pass operation to extinction, it is necessary to control the amount of polycyclic hydrocarbons in the feed and coming in contact with the crystalline aluminosilicate portion of the catalyst in the hydrocracking zone. Otherwise, the polycyclic hydrocarbon concentration will steadily increase in the recycle stream recovered from the hydrocracking zone and, when recycled thereto, will adversely affect the cracking selectivity and activity of the crystalline aluminosilicate-base catalysts. In the case of amorphous-base hydrocracking catalysts, it is principally their activity in the second stage that is adversely affected under hydrocracking conditions by excessive concentrations of polycyclic aromatic hydrocarbons.

The build-up of polycyclic aromatic hydrocarbons, for example, three or more condensed ring compounds, in the hydrocracking stage causes increased catalyst aging rates therein and thereby necessitates more frequent catalyst regenerations. On the other hand, the catalyst employed in the raw feed pretreating-hydrogenation zone is much less rapidly deactivated by nitrogen and condensed ring polycyclic aromatic hydrocarbon compounds when operated at selected pretreating conditions than either an amorphous-base hydrocracking catalyst, a crystalline aluminosilicate-base hydrocracking catalyst or a mixture thereof when employed at hydrocracking conditions. Thus, generally, pretreating catalysts need not be regenerated as frequently as hydrocracking catalysts, but as both stages of pretreating and hydrocracking are in a single train, when the catalyst in one stage is being regenerated, the entire process sequence must be shut down. When it is necessary to regenerate the catalyst in only one stage to provide process downtime therefor, substantial economic disadvantages for the process are introduced. Greater process efficiency and thus substantially improved economics will result if the regeneration of both the hydrogenation-pretreating catalyst and the hydrocracking catalyst are accomplished simultaneously since more efficient use is made of the process capacity. It is thus desirable to improve process efficiency by decreasing the aging rate of the hydrocracking catalyst to a value commensurate with that of the pretreating-hydrogenation catalyst.

At the present time, hydrocracking catalyst aging rates are improved by selecting stocks having a limited concentration of polycyclic aromatic hydrocarbons therein.

This feed selection, however, introduces considerable process disadvantages by reducing the flexibility of the process for converting a wide variety of hydrocarbon feeds. Furthermore, as the hydrocracking catalyst activity is reduced during on-stream time, its ability to convert polycyclic aromatic hydrocarbons is significantly reduced and the permissible amount of polycyclic aromatic hydrocarbons in the charge will vary with on-stream time. While the hydrocracking catalyst may be sufficiently active initially to convert the hydrocarbons in the feed other than those of the polycyclic aromatic type, this activity will be rapidly impaired by the condensed ring component of the polycyclic aromatics in the feed and an undesirable build-up of insufficiently converted hydrocarbons and polycyclic aromatic hydrocarbons in the recycle stream will result. Thus, it will become necessary to regenerate the hydrocracking catalyst more often than desired to maintain its activity for hydrocarbon conversion including polycondensed aromatic hydrocarbons.

SUMMARY OF THE INVENTION

In accordance with the present invention, a petroleum hydrocarbon fresh feed material boiling within the range of from about 400° F. to about 1100° F. and containing nitrogen, sulfur and polycyclic compounds of three or more condensed ring components is passed sequentially through a first feed hydrogenation-pretreating zone and then through at least one second hydrocracking zone in the presence of a suitable hydrocracking catalyst. The effluent from the hydrogenation-pretreating zone is separated to recover hydrogenated and partially cracked hydrocarbons from unreacted hydrogen, ammonia, water and hydrogen sulfide. Separated hydrogen may be recycled to the process as desired. The hydrocarbon stream obtained from the pretreated separation step of acceptable polycyclic aromatic concentration is then directed to hydrocracking treatment in one or more separate hydrocracking zones wherein it is further converted to lower boiling products such as gasoline. The hydrocracking effluent is separated to separately recover lower boiling desired products from a high-boiling recycle stream comprising unreacted or partially converted hydrocarbons including polycyclic aromatic constituents. The recycle stream of the hydrocracking step may be combined as desired with the hydrocarbon effluent obtained from the feed pretreating-hydrogenation zone to form the acceptable hydrocarbon feed passed to the hydrocracking zone.

The effluent of the hydrogenation-pretreatment step, the hydrocracking recycle stream and the raw fresh feed to the process are monitored substantially continuously or intermittently as desired so as to identify the concentration of condensed ring polycyclic aromatic hydrocarbons having more than three and preferably from about 3 to about 7 unsaturated condensed rings therein. The measurements thus obtained are then used to control conditions in the hydrocarbon feed pretreating-hydrogenation zone in a manner to limit the concentration of polycyclic aromatic hydrocarbons from building up in the hydrocracking step. The concentration of polycyclic aromatic condensed ring compounds as measured by the maximum in the most prominent peak of the visible and ultraviolet spectrum between about 3000 and about 5000 angstroms is limited in the hydrocarbon stream passed to the hydrocracking zone to the following ranges. If that stream contains polycyclic condensed-ring aromatic compounds which significantly absorb light between about 4000 and about 5000 A., the concentration of those compounds is limited to not more than 350 p.p.m. and preferably the concentration is maintained at less than about 100 p.p.m. If, on the other hand, the stream does not contain polycyclic condensed-ring aromatics which absorb light significantly between about 4000 and about 5000 A., then the concentration of polycyclic condensed-ring aromatics which absorb light between about 3000 and about 4000 A. is used for control and is limited to not more than

10,000 p.p.m. and preferably the concentration is maintained at less than about 1000 p.p.m.

A comment about asborption of light by aromatics seems appropriate at this point in the discussion because it helps to explain some apparent wordiness required for precision in the discussion herein presented. For example, the polycyclic aromatic compound phenyl perylene contains 6 aromatic rings. Five are condensed aromatic rings (i.e. rings having at least 2 carbon atoms common to one another) and one is an uncondensed aromatic ring (i.e. a ring attached to but having no carbon atom or atoms in common with another ring). This compound absorbs light (1) as an aromatic having 5 condensed rings and (2) as a single ring aromatic. However, it does not absorb light near the wave length at which corresponding 6 condensed-ring aromatic compounds absorb light. In matters related to absorption spectroscopy, therefore, a reference to a polycyclic aromatic generally in this specification does not identify the particular number of condensed-ring constituents. A reference to an *x*-ring polycyclic aromatic, the other hand, means only that the aromatic has *x* condensed rings; it does not means that the aromatic only has *x* rings; it may or may not have more than *x* rings. Thus in an effort to clearly identify applicants' invention and in view of the effect of condensed-ring structures on light absorption spectroscopy, the present application is directed primarliy to referring to polycyclic aromatic compounds in terms of their condensed-ring structure.

It is to be understood that the pretreating-hydrogenation zone and the hydrocracking zones of the present invention may be maintained within one or more reactors.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 presents diagrammatically one arrangement of process steps for practicing the method of this invention comprising a hydrogenation-pretreat step followed by a hydrocracking step wherein different streams can be analyzed for condensed ring polycyclic aromatic hydrocarbons.

FIG. 2 presents a plot of data arranged to show the effect of reactor temperature on aromatics and nitrogen content of the pretreating stage effluent.

FIG. 3 presents a plot of data arranged to show a relationship between pretreating stage performance with catalyst aging rate in the subsequent hydrocracking stage.

DESCRIPTION OF SPECIFIC EMBODIMENTS

It has been found that by controlling the feed pretreating-hydrogenation conditions in response to the concentration of polycyclic aromatics of three or more condensed-ring structures tolerable in the hydrocarbon feed stream passed from the pretreating-hydrogenation step to the hydrocracking step that the hydrocracking catalyst can be more efficiently used for effecting the conversion of the hydrocarbon charge to lower boiling desired products. Furthermore, by controlling the severity of the pretreating conditions in accordance with this invention there is provided a convenient method for improving the hydrocracking catalyst aging rate without adversely affecting the process throughput rate. Thus, the present invention provides a convenient method and process which closely controls the catalyst aging rates in each of a pretreating-hydrogenation step and one or more subsequent hydrocracking steps. In one embodiment of the invention, this control is employed so that the catalysts of all stages will be in a condition to be regenerated simultaneously and thus eliminate the need for additional proces down-time to separately regenerate only one of the catalysts. Therefore it can be seen that the method and process of this invention provides substantially economic advantages over presently known hydrocracking processes.

The hydrogenation-pretreating catalyst employed in the process of this invention generally comprises a hydrogenation component dispersed on an amorphous-base and is generally characterized as a catalyst of relatively mild

cracking activity and greater hydrogenating activity as compared to an amorphous or crystalline aluminosilicate containing hydrocracking catalyst. Depending upon the activity of the pretreating-hydrogenation catalyst, the reaction in the pretreating-hydrogenation zone can be either rate controlled or controlled by the hydrogenation-dehydrogenation equilibrium. For a given pressure and contact time in the pretreating-hydrogenation zone, the concentration of polycyclic aromatic hydrocarbon in the effluent therefrom depends upon (1) temperature and (2) whether the reaction in the pretreating-hydrogenation zone is controlled by the rate of reaction or by the hydrogenation-dehydrogenation equilibrium. In such a system, when the reaction is rate-controlled, the concentration of polycyclic aromatic hydrocarbons can be reduced by either increasing the temperature or decreasing the space velocity. When the reaction is controlled by the hydrogenation-dehydrogenation equilibrium, on the other hand, the concentration of polycyclic aromatic hydrocarbons in the hydrogenation zone effluent is reduced by decreasing temperature. Whether the reaction is rate-controlled or equilibrium-controlled, the concentration of polyclclic aromatic hydrocarbons in the hydrogenation stage effluent can be reduced by increasing the hydrogen partial pressure and/or reducing the oil partial pressure in the hydrogenation-pretreating zone. When the reaction is rate-controlled, reducing the temperature will cause the rate of conversion of the polycyclic aromatics to be reduced. This is undesirable since the concentration of polycyclic aromatic hydrocarbons is increased thereby. However, when the reaction is at equilibrium, a temperature increase will be undesirable since the polycyclic aromatic concentration will increase. Therefore, at a given hydrogen partial pressure and contact time operating at the lowest possible temperature at which the reaction is equilibrium-controlled will reduce to a minimum the concentration of polycyclic aromatics in the pretreating-hydrogenation effluent.

As stated above, the concentration of polycyclic aromatic hydrocarbons comprising three or more condensed-ring constituents and found in the pretreating-hydrogenation stage hydrocarbon effluent can be reduced by increasing hydrogen partial pressure during hydrogenation thereof. However, the pretreating-hydrogenation reactors are built to withstand a certain maximum pressure which is usually dictated by the economics of the process and the advantages to be gained by the increased pressure versus the cost of building the reactor of increased strength. Therefore, within the limits of a particular process design, the hydrogen partial pressure can be conveniently increased in the pretreating step by increasing the hydrogen circulation rate therein. In addition, the concentration of polycyclic aromatic hydrocarbons in the effluent can be significantly reduced by regulating the temperature and space velocity in the manner described herein. It is also within the scope of this invention to regulate the concentration of polycyclic aromatics found in the raw fresh feed to the pretreating step of the process in combination with the above-described process, thus utilizing a concept of this invention known and identified as feed forward control of the process.

In the process of the present invention, any one of a number of known methods can be employed for ascertaining the concentration and number of polycyclic aromatics in a given hydrocarbon stream. Absorption spectroscopy is presently known as one convenient method for identifying the concentration of condensed-ring polycyclic aromatic hydrocarbons in a hydrocarbon stream. The process of this invention will be specifically described hereinafter in detail with reference to such a method of detection.

In accordance with this invention it has been found that the polycyclic aromatic hydrocarbons of which the concentration should be controlled are those having three or more, and preferably less than seven condensed-ring constituents in the hydrocarbon structure. These condensed rings can be substituted with either aliphatic or aromatic moieties or can be substituted with heterocyclic rings. Polycyclic aromatic hydrocarbons of three or more condensed rings have very intense adsorption bands in the visible and ultraviolet regions of the electromagnetic spectrum in the range of from about 2000 to about 7000 A. The portion of the electromagnetic spectrum in the ultraviolet and visible regions which is of particular interest in the present context is in the range of from about 3000 to about 5500 A. Those polycyclic aromatic hydrocarbon condensed-ring structures which are the most critical in the process of this invention have very intense adsorption bands in the ultraviolet and visible electromagnetic wavelength range of about 3220 A., 3370 A., 3780 A., 4340 A., 4480 A., 4820 A. and 5225 A. The absorption bands of the pertinent polycyclic aromatic species will be influenced by petroleum feed materials which contain mixtures of compounds of close chemical relationship and by chromophoric chemical groupings in the feed mixtures. However, the characteristic absorption bands are sufficiently intense to be easily identified by those skilled in the art. The theory of absorption spectroscopy is well defined at present. It is reviewed in such treatises as "Ultraviolet and Visible Spectroscopy" by Orchin and Friedel, and will be referred to only briefly herein.

When an organic molecule is exposed to a continuous spectrum of electromagnetic radiation, radiation having certain wavelengths is absorbed, causing excitation of the molecule to a higher energy state. The energy difference between the lower and higher energy states determines the wavelength of the absorbed light. Many factors influence the differences between energy states. The spectra to be dealt with in the present invention are adsorption spectra which result largely from transitions of the electrons of molecules to various energy states. According to quantum mechanics, these energy states have discrete values corresponding to integral multiples of a unit of energy. The values of these discrete quantum mechanical energy levels depend on the molecular structure of the absorbing species. For example, certain polycyclic aromatic hydrocarbons in petroleum absorb strongly at very specific wavelengths in the visible and ultraviolet region and exhibit a unique absorption pattern.

According to Beer's Law, the amount of light absorbed in a layer is proportional to the number (concentration) of absorbing molecules in a layer of absorbing material. According to Lambert's Law, the amount of light absorbed is proportional to the thickness of the layer. The combination of these two laws is expressed mathematically as follows:

$$\frac{I}{I_0}=10^{-Kcb}=\frac{10^{-(Ecb)}}{M}$$

I=Transmitted light intensity
I_0=Incident light intensity
E=Molar extinction coefficient
b=Cell thickness, i.e. layer thickness
c=Concentration of the absorbing species
M=Molecular weight

The quantity

$$K\left(=\frac{E}{M}\right)$$

is the "specific extinction coefficient." The technique of absorption analysis is to determine the K value of an absorbing material by determining the average value of I/I_0 at several wavelengths of the whole spectrum. The apparent K value of a mixture of an absorbing with a non-absorbing material is proportional to the concentration of absorbing material. Thus, for example, when it is desired to know the amount of polycyclic aromatics absorbing at 4340 A. in an otherwise transparent diluent, the apparent K value is proportional to the cencentration of those aromatics. On the other hand, the K value of a

mixture of materials absorbing at 4340 A., for example in an otherwise transparent diluent, depends on some combination of the K values of the individual components of that mixture. When that mixture is approximately constant in composition, the amount of absorption is proportional to the concentrations of mixed aromatics.

A system of instrumentation which may typically be used in this invention, is the "Du Pont 400 photomertic analyzer." This instrument is fully described in a series of publications by the Instrument Products Division of the Du Pont Company. The sample stream flows continuously through the sample cell. The term split-beam refers to the division of the incident diffuse light into reference and measuring beams after light has passed through the sample. In a typical arrangement, radiation from a selected light source passes through the sample and then to a photometer unit where it is split by a semi-transparent mirror into two beams. One beam is directed to the measuring photometer through an optical filter which removes all wavelengths except the measured wavelength. This wavelength is strongly absorbed by this sample. The second beam falls on the reference photoelectric tube after passing an optical filter which transmits only the reference wavelength. The latter is absorbed only weakly or not at all by the constituent in the sample cell. The photoelectric tubes translate these intensities to proportional elecrical currents in the amplifier. In the amplifier, correction is made (by logarithmic amplifiers) for the logarithmic relationship between the ratio of the intensities and concentration (or thickness) in accordance with Beer's and Lambert's Laws. The output of the logarithmic amplifier is, therefore, linear with sample concentration. Use of the split-beam technique implies that changes in light source intensity during analysis, or the presence of bubbles or particulate matter sample cell have virtually no effect on the accuracy of the analysis. The presence of any extraneous matter will bias both the reference and measuring wavelengths equally. Online analyses can be conducted at pressures up to 750 p.s.i. and temperatures up to 700° F. Sample cell thickness range from .002 inch to 24 feet. Response times as low as about .001 second can be attained with suitable cell design. Additional information regarding ultraviolet instrumentation can be found in "Ultraviolet Spectra of Aromatic Compounds" by Friedel and Orchin. It is within the scope of this invention to employ either continuous or intermittent process control.

While the present invention will be discussed in detail with reference to methods of analysis comprising absorption spectroscopy, it is to be understood that other available methods for determining the concentration of polycyclic or poly-condsensed aromatic hydrocarbons generally, or those of 3 to 7 condensed-ring structures, can be employed with equal facility. Suitable analytical methods which can be employed either alone or in combination are gradient elution chromatography, mass spectrometry, infrared absorption spectroscopy, gas-liquid chromatography and magnetic resonance including nuclear resonance, electron paramagnetic resonance and quadruple resonance.

The operating conditions employed in the process of the present invention depend upon the particular catalysts employed in the various steps of the process. Each catalyst composition has, for example, a particular aging rate which is dependent upon its interaction with the type of feed employed and the reaction conditions employed. For example, zeolite-base hydrocracking catalysts have relatively high aging rates in the presence of relatively high concentrations of polycyclic aromatic hydrocarbons, having several condensed rings and lower aging rates in the presence of organo-nitrogen compounds, as compared with an amorphous-base hydrocracking catalyst. Therefore, the operating conditions in the pretreat-hydrogenation step will vary depending upon the catalyst employed, the hydrogenation conditions most suitable for the catalyst and the feed employed. It is desirable however to vary the conditions in the hydrogenation feed pretreat step so that the catalysts in each of the hydrogenation step and the subsequent hydrocracking step will require regeneration at or about the same time. This can be effected by determining the catalyst aging rate with a particular hydrocarbon feed and then suitably regulating the pretreating-hydrogenation step conditions. In place of or in addition to the pretreater feed monitoring, the component feed streams employed to make up the pretreater feed can also be monitored for feed forward control of the pretreater; and the blending of these streams can be controlled by said monitoring. The process of the present invention can be controlled manually, or automatically such as by a computer control which is responsive to the visible and ultraviolet measurements for undesired polycyclic material above identified and obtained, whether measured continuously or intermittently.

The process of the present invention can also be monitored and controlled by measuring the concentration of condensed-ring polycyclic aromatic hydrocarbons in (1) the feed to the pretreating-hydrogenating step, (2) the recycle stream of the subsequent hydrocracking stage or stages, (3) the hydrocracking-stage feed stream made up of both the recycle stream and the hydrogenation step effluent stream, or any one of these streams alone or in combination with another as discussed above. More precise process control can be obtained by measuring the concentration of condensed-ring polycyclic aromatics in all three streams. It is within the scope of this invention to measure the concentration of polycyclic aromatics in the raw feed charged to the pretreating-hydrogenation zone and to adjust the feed composition in this respect in order to obtain approximately equal catalyst on-stream time and deactivation in all the reaction stages.

The amorphous-base hydrogenation-pretreating catalyst employed comprises one or more hydrogenation components dispersed in and on an amorphous-base having cracking activity and pores of a size above about 20 A., and preferably between about 30 and about 500 A. The hydrogenation components which can be employed therewith include the Group VI–B and Group VIII metals of the Periodic Table as well as their oxides, their sulfides, or mixtures thereof. The Group VI–B metals which can be employed include chromium, molybdenum and tungsten while the Group VIII metals which can be employed include iron, nickel, cobalt, the platinum type metals such as platinum, iridium, osmium; the palladium type metals such as palladium, rhodium and ruthenium and mixtures thereof. Among the preferred hydrogenation components are included nickel-tungsten sulfide, nickel sulfide, cobalt-molybdenum sulfide, nickel-cobalt-molybdenum sulfide, platinum and palladium sulfides, and platinum and palladium. The amorphous-base components which can be used therewith include the oxides of metals of Groups II–A, III–A, and IV–B of the Periodic Table as well as silica or mixtures thereof. Examples of amorphous bases which can be employed include silica-alumina, silica-zirconia, silica-zirconia-alumina, silica-magnesia, silica, alumina and the like. The amorphous-base components employed are those having a cracking activity index between about 15 and about 45 and preferably between about 20 and about 35 as measured by the "Cat A" test described by Alexander and Shimp in National Petroleum News, 36 page R–537 (Aug. 2, 1944), and these specifications obtain before the catalyst has been contacted with ammonia or nitrogen-containing organic compounds at hydrocracking conditions.

The hydrogenation metal component of the pretreating catalyst is employed in amounts and under conditions selected to effect substantial hydrogenation reaction; that is, hydrogenation in amounts sufficient to convert a substantial majority of any organic nitrogen and sulfur compounds in the feed to ammonia and hydrogen sulfide respectively. It is important to this invention that the hydrogenation activity be sufficient to convert a substantial

proportion of the polycyclic condensed aromatic compounds to the corresponding saturated compounds. The amount of hydrogenation component employed in the pretreating catalyst depends upon the hydrogenation activity of the particular component employed and comprises from about 0.1 to about 45 weight percent, based upon the weight of the amorphous cracking base. When nickel or metals such as platinum or palladium are employed, preferably from about 0.1 to about 6 weight percent and more preferably from about 0.2 to about 2 weight percent are used based upon the weight of the amorphous base. When the hydrogenation component is other than nickel, platinum or palladium, it is preferred to employ from about 8 to about 50 weight percent thereof calculated as metal oxides and based upon the weight of the amorphous base. The hydrogenation component can be introduced into the amorphous base by impregnation, by coprecipitation on the base surface, by admixture, by ion exchange or by other methods well-known in the art.

In the hydrogenation-pretreating step, the temperature is maintained in the range of between about 600° F. and about 900° F., preferably between about 650° F. and about 800° F., a hydrogen partial pressure in the range between about 1000 p.s.i.g. and 3500 p.s.i.g., preferably about 1500 p.s.i.g. and about 2500 p.s.i.g., with a liquid hourly space velocity between about 0.2 v./hr./v. and about 5/v./hr./v., and a hydrogen circulation rate of between about 1000 s.c.f./b. and about 20,000 s.c.f./b., preferably between about 5000 s.c.f./b. and about 10,000 s.c.f./b.

The hydrocracking catalysts employed herein may comprise one or more hydrogenation components in combination with a support material having cracking activity such as a silicious cracking base, a crystalline aluminosilicate material or mixtures thereof having cracking activity. It is to be understood that while the crystalline aluminosilicate cracking component can be employed alone or as the sole support for the hydrogenation component, it can also be employed in association with an amorphous silicious cracking base such as described below. The ratio between the amount of crystalline aluminosilicate material and amorphous cracking base may vary considerably depending upon the activity of each and may be in a range of from about 0 to 100% and preferably from about 3 to about 80%.

The crystalline aluminosilicate cracking component of the hydrocracking catalyst is structurally characterized by having uniformly dimensioned pores formed by alumina and silica tetrahedra. For purposes of the present invention it is desirable to employ crystalline aluminosilicates having pore size openings between about 6 A. and 15 A.

Both synthetic and naturally occurring crystalline aluminosilicate materials may be used. Among those which may be used are the synthetic crystalline aluminosilicates such as zeolites X, Y, B, L and T, and naturally occurring materials such as faujasite, mordenite, chabazite, erionite, offretite, and others. These aluminosilicates are preferably used in a form characterized by a low sodium or alkali metal content, below about five weight percent, and preferably below about two weight percent, calculated as alkali metal oxide, based upon the weight of the aluminosilicate.

Such materials are prepared by base exchange with fluid containing metal-bearing ions which are exchangeable with sodium or other alkali metal ions in the manner described in Plank et al., U.S. patents, 3,140,249, 3,140,253 and others to obtain a selective cracking catalyst of high activity. Among the metallic cations which can be so introduced to enhance the cracking activity of the aluminosilicate are those of the Groups I–B through VIII of the Periodic Table, as well as the rare earths. Also, the alkali metal can be removed from the aluminosilicate by base exchanging with a hydrogen-containing cation such as the ammonium or the tetraalkylammonium ion followed by treatment to obtain the catayst in the hydrogen form. Further the aluminosilicate can be base exchanged in a manner to replace the alkali metal cation with a mixture of the above metal cations or a mixture of the above metal cations with hydrogen cation. The preferred forms of the crystalline aluminosilicate are those containing rare earth metal cations, rare earth metal cations and hydrogen cations, palladium ions or nickel cations and hydrogen ions, palladium ions or nickel cations and rare earth cations, palladium ions or nickel cations and rare earth ions and hydrogen ions, since these forms of the material exhibit high cracking activity and good selectivity. The remaining alkali metal content, calculated as metal oxide should be below about 5 weight percent and preferably below about 2 weight percent to obtain the desired cracking activity and selectivity.

The amorphous-base component of the hydrocracking catalyst is characterized by having a higher hydrocracking activity than that of the pretreating catalyst, a pore size above about 20 A., and preferably of a size in a range selected from about 30 and about 500 A. The amorphous-base cracking components which can be used herein include the oxides of metals of Groups II–A, III–A, and IV–B of the Periodic Table as well as silica or mixtures thereof. Examples of amorphous silicious cracking bases which can be employed herein include silica-alumina, silica-zirconia, silica-zirconia-alumina, silica-magnesia, silica, alumina and the like. The amorphous-base components employed herein are those having a cracking activity index between about 20 and about 60 and preferably at least about 30 as measured by the "Cat A" test described by Alexander and Shimp in National Petroleum News, 36 page R–537 (Aug. 2, 1944).

The hydrogenation metal component of the hydrocracking catalyst may be employed in amounts in the range of from about 0.1 to about 45 weight percent thereof based upon the weight or amount of the cracking component, the type of cracking component and the hydrogenation metal employed. The hydrogenation component may be introduced into the cracking component by ion exchange, by impregnation, as a physical admixture, or by other methods known to the art.

Nickel or metals such as platinum or palladium are employed in amounts preferably from about 0.1 to about 6 weight percent, and more preferably from about 0.2 to about 3 weight percent, based upon the weight of the zeolitic base. When the hydrogenation metal component is other than nickel, platinum or palladium, it is preferred to employ from about 6 to about 30 weight percent thereof, calculated as metal oxides and based upon the crystalline aluminosilicate cracking base weight and from about 8 to about 50 weight percent calculated as metal oxides and based on the amorphous cracking catalyst base weight. Hydrogenation components such as nickel sulfide and tungsten sulfide mixtures in amounts of between about 5 and about 15 weight percent of the nickel and tungsten metals, platinum in amounts of from about 0.1 and about 5 weight percent combined with a zeolite X or a zeolite Y containing rare earth, hydrogen, or a mixture of rare earth and hydrogen cations in combination with a silicious cracking base are very effective hydrocracking catalysts.

The hydrocracking conversion conditions are selected so as to effect conversion of the hydrocarbon feed in the range of from about 20 to about 80 volume percent perpass to products boiling below 400° F. Generally, conditions are maintained at a temperature in the range of from about 450° F. to about 900° F., preferably from about 550° F. to about 750° F.; a hydrogen partial pressure in the range of from about 500 p.s.i.g. to about 3,000 p.s.i.g., preferably from about 1,000 p.s.i.g. to about 2,500 p.s.i.g.; a space velocity in the range of from about 0.1 to about 10 v./hr./v. and preferably from about 1 to about 5 v./hr./v., and at a hydrogen circulation rate in the range of from about 1,000 to about 20,000 s.c.f./b. and preferably from about 3,000 to about 8,000 s.c.f./b.

The hydrocarbon feeds which can be processed by this invention to advantage are those distillates boiling in the range of between about 400° F. and about 1100° F. or residual fractions which are essentially free of ash and asphaltic constituents. Hydrocarbon feeds which can be employed include virgin heavy vacuum gas oils, coker gas oils, gas oil from catalytic cracking processes, the heavy aromatic extracts obtained by furfural extracting high boiling hydrocarbons such as light, medium, and heavy virgin gas oils, cracked gas oils, or mixtures thereof.

FIG. 1 presents diagrammatically one arrangement of process steps for practicing the method of this invention comprising a hydrogenation-pretreat step followed by a hydrocracking step.

FIG. 2 presents a plot of data arranged to show the effect of reactor temperature on aromatics and nitrogen content of the pretreating stage effluent.

FIG. 3 presents a plot of data arranged to show a relationship between pretreating stage performance with catalyst aging rate in the subsequent hydrocracking stage.

Referring to FIG. 1 by way of example a fresh gas oil feed containing polycyclic aromatics is introduced to the process by conduit **2**. The hydrocarbon fed may be mixed with a hydrocarbon stream having a relatively higher concentration of polycyclic aromatics introduced by conduit **4**. The resultant hydrocarbon feed is directed through conduit **6** to a heater **8** wherein it is preheated to an elevated temperature suitable for use in the pretreating-hydrogenation step. The preheated feed is recovered from heater **8** and thereafter passed to pretreating-hydrogenation reactor **10** by conduit **12**. In pretreating-hydrogenation reactor **10**, the fresh feed is reacted with hydrogen introduced to the process by conduit **14**. The organo-nitrogen and sulfur compounds in the hydrocarbon feed passed to reactor **10** are converted to ammonia and hydrogen sulfide respectively. Polycyclic aromatics compounds in the hydrocarbon feed are saturated and some cracking of the charge is also effected. The effluent of the pretreating-hydrogenation reactor **10** is removed through conduit **16** and directed to a separator **18**. Hydrogen rich gas is removed from separator **18** through conduit **20** for recycle to the process. Fresh hydrogen rich gas in conduit **22** may be combined with the recycle gas in conduit **20** and the resultant mixture thus formed directed to the hydrogenation-pretreating reactor through conduit **14**. The remaining effluent is removed from hydrogen separator **18** and directed through conduit **24** to a stripping unit **26** wherein ammonia, hydrogen sulfide and water are separated for removal through conduit **28**. The hydrogenated hydrocarbon stream from which nitrogen and sulfur compounds have been removed is withdrawn from stripping unit **26** through conduit **30**, mixed with recycle hydrocarbons from conduit **32** and directed through conduits **34** and **48** to hydrocracking reactor **36**. In hydrocracking reactor **36**, the hydrocarbons except for aromatic moieties are converted under hydrocracking conditions to lower boiling hydrocarbons. The effluent from hydrocracking reactor **36** is removed through conduit **38** and directed to a separation zone **40**. In separation zone **40**, the product effluent of hydrocracking is separated to recover a hydrogen rich recycle stream, unconverted hydrocarbons, and gasoline product material. Gasoline product material is recovered through conduit **42**. It is to be understood that several different product materials may be recovered in addition to gasoline, such as jet fuels and fuel oils. The unconverted hydrocarbons boiling above the product boiling range materials obtained from separation zone **40**, is removed through conduit **32** and combined with the hydrogenated feed in conduit **30** for passage to reactor **36** by conduits **34**. Hydrogen rich gas in conduit **44** is mixed with fresh hydrogen rich gas introduced through conduit **46** and the resultant mixture is directed through conduit **48** to hydrocracking reactor **36**.

In the arrangement of FIG. 1 provisions are made for determining the concentration of polycyclic aromatics in any one of four streams. Samples of the hydrocarbon feed in conduit **34** are taken through line **50**. Samples of the hydrocarbon feed in conduit **32** are taken through line **52**. Samples of the hydrocarbon feed in conduit **30** are taken through line **54**. Samples of the hydrocarbon feed in conduit **6** are taken through line **56**. Each of the hydrocarbon streams may be analyzed for polycyclic aromatic concentration at the analysis step **58**, and the information obtained is then directed to process control **60**. Signals from process control **60** can be directed to vary the temperature, space velocity, hydrogen partial pressure or type of feed passed to the pretreating-hydrogenation reactor. The hydrogen partial pressure may be varied by opening or closing valve **62** in response to a signal through line **64**. The space velocity in hydrogenation reactor **10** may be varied by opening or closing valve **66** in response to a signal passed through line **68** and **70**. The temperature of the feed preheat and thus the hydrogenation reactor **10** may be varied by controlling valve **72** which supplies combustion fuel through conduit **74** to the preheater **8**. The valve **72** is controlled in response to a signal from control **60** through lines **68**, **76** and **78**. The polycyclic aromatic concentration in the fresh feed in conduit **12** is varied by opening or closing valve **80** in response to a signal obtained from control **60** through lines **68** and **76**. The signals from control **60** can be directed to the desired valves in any manner as for example electronically, pneumatically, or mechanically.

Referring now to FIG. 2 by way of example, there is shown graphically the relation that has been found to exist between the temperature employed in the hydrogenation-pretreating stage and the condensed-ring polycyclic aromatics content of the stabilized liquid effluent obtained therefrom as indexed by absorption of light at a wavelength of about 4480 A. by that effluent. There is also graphically shown in FIG. 2 the relation that was found to exist between temperature in the hydrogenation-pretreating stage and the organically combined nitrogen content of the hydrogenation-pretreater effluent. The graphical representation of FIG. 2 is based on data obtained from processing a charge stock boiling in the range of from about 550° F. to about 950° F. and comprising a mixture of coker gas oils, catalytic cracking cycle stocks and an "aromatic" fraction obtained from furfural extraction of a heavy catalytic cracking cycle stock. This charge stock contained about 1000 p.p.m. by weight of organically combined nitrogen, and it was processed over a commercial pretreating catalyst at 2000 p.s.i.g. total pressure, 1.2 liquid hourly space velocity, and 7000 s.c.f. of hydrogen circulation per barrel of liquid feed.

FIG. 2 shows that there is not a one-to-one correspondence between the condensed-ring polycyclic aromatics content and the organically combined nitrogen content of the hydrogenation-pretreater effluent. Rather it is shown that at a given condensed-ring polycyclic aromatics content, there can be two different nitrogen contents depending on whether the pretreater effluent was made at a temperature to the right or to the left of that corresponding to the minimum in the graph of polycyclics content as a function of reactor temperature in FIG. 2. Point A on the curve of FIG. 2 represents the lowest temperature at which hydrogenation-dehydrogenation equilibrium is obtained for the catalyst employed. When the hydrogenation-pretreating reactor is operated in a manner wherein the rate of reaction is controlling, the temperature-concentration relationship is represented by the curve to the left of Point A. When operating under these conditions, the polycyclic aromatic condensed-ring concentration can be decreased by either increasing temperature or decreasing space velocity. On the other hand, when the reaction in the pretreating-hydrogenation reactor is controlled by the hydrogenation-dehydrogenation equilibrium, the temperature-concentration relationship is represented by the curve to the right of Point A. When operating under these conditions, the polycyclic aromatic condensed-ring

concentration can be reduced by decreasing temperature.

Referring now to FIG. 3, there is shown graphically a relationship that exists between the intensity with which the stabilized effluent liquid from the first-stage hydrogenation-pretreater absorbs light at a wavelength of 4480 A. and the catalyst aging rate in a subsequent hydrocracking step. The data obtained with two different catalysts are presented; one catalyst being formed of an amorphous-base having cracking activity as support for the hydrogenation component, and the other comprising a mixture of an amorphous-base having cracking activity and a crystalline-aluminosilicate base having cracking activity being used as support for the hydrogenation component. The intensity of absorption of the light at 4480 A. by the pretreater effluent obtained from each of the catalysts is plotted, for convenience, as 1000 times the light absorption factor at that wavelength. The charge stocks used to produce the data reflected in FIG. 3 were all liquid effluents containing about 1 p.p.m. by weight of organically combined nitrogen obtained by the pretreating-stage operation under the conditions and with the pretreating catalyst of FIG. 2. The temperature at which the charge stocks for FIG. 3 were obtained varied with pretreating catalyst age (e.g. time the pretreater was on stream and/or degree of catalyst deactivation). Depending on that temperature, the charge stocks of FIG. 3 had different polycyclic aromatics contents even though they all had 1 p.p.m. by weight of organically combined nitrogen.

All the results represented in FIG. 3 are for 1 p.p.m. N in the pretreater effluent; it is therefore apparent that the specification of the nitrogen content of the liquid effluent of the pretreating stage is not sufficient of itself to guarantee control over the catalyst aging rate in the subsequent hydrocracking stages. Particularly, it has been shown that, at a fixed nitrogen content or level in the pretreater effluent, catalyst aging in a subsequent hydrocracking stage depends on the polycyclic aromatics content, as indexed by light absorption, of that effluent; and that dependence on polycyclic aromatics content has been found to vary from catalyst to catalyst.

To illustrate our invention more clearly, it will be assumed that a catalyst aging rate of not more than 0.3° F. per day is desired in the hydrocracking stages of the process. From FIG. 3 we find that we must operate the preceding pretreating stage to produce an effluent product having a light absorption factor of not more than 3×10^{-3} if we use the amorphous-base catalyst shown in FIG. 3 in the hydrocracking stages of the process, and of not more than 8×10^{-3} if we use the mixed crystalline-amorphous base catalyst of FIG. 3 in the hydrocracking stages of the process. Suppose that we use the amorphous-base catalyst in the hydrocracking stages of the process. Then we find from FIG. 2 that satisfactory pretreating-stage effluent can be made at temperatures between 675° F. and 715° F. under the conditions of FIG. 2 with the catalyst of FIG. 2 at the degree of aging which that catalyst had experienced when the data of FIG. 2 were obtained. However, as the catalyst of FIG. 2 ages further, the line representing nitrogen content in FIG. 2 will shift to the right; the descending leg of the U-shaped curve of light absorption factor will shift to the right whereas the ascending leg of that curve will remain fixed; and the minimum value of the absorption factor will slowly increase. Thus, as the pretreating catalyst ages, the lower limit of the temperature ranges corresponding to satisfactory pretreating stage effluent will increase while the upper limit will remain constant, and the temperature range for satisfactory pretreating will become correspondingly narrower.

From the foregoing, it will be evident that the quantitative numerical results presented in FIG. 2 change as the pretreating-stage catalyst ages, and therefore cannot be used per se to insure production of satisfactory pretreater effluent throughout the total life of the pretreating catalyst. The qualitative aspects of the results in FIG. 2, however, do indicate the method of this invention for producing a pretreating-stage effluent of a quality and composition, at least with respect to the polycyclic aromatic condensed-ring concentrations, which will be satisfactory as hydrocracking-stage feed. As we noted before, FIG. 3 shows that we must operate the pretreating stage to produce an effluent having a light absorption factor of not more than 3×10^{-3} if we use the amorphous-base catalyst of FIG. 3 at an aging rate of 0.3° F. per day in the hydrocracking stages under the conditions of FIG. 3. Assuming for purpose of illustration that our visible and ultraviolet light monitor on the pretreating-stage effluent shows that the effluent has an absorption factor of 4×10^{-3}, we are not able to use this information quantitatively with respect to FIG. 2 because our pretreating catalyst is not necessarily at the same age as it was when the data of FIG. 2 were obtained. However, we do know from FIG. 2 that raising pretreating-stage temperature will bring a desired reduction in the light absorption factor if the result given by the light absorption monitor lies on the descending leg of the U-shaped curve of FIG. 2. Therefore, either manually or automatically, and as a generated function of the light absorption factor, we can raise the pretreating-stage temperature and watch for a suitable effect on the light absorption factor of the pretreater effluent. If the absorption factor comes down, we continue raising temperature until the absorption factor just falls to 3×10^{-3}, at which point the pretreater effluent will be satisfactory as a hydrocracking-stage feed insofar as hydrocracking catalyst aging is concerned. If, on the other hand, the absorption factor goes up as temperature is raised, we know that we are on the ascending leg of the U-shaped curve of FIG. 2. Then, we must drop the pretreating temperature until the absorption factor just falls to 3×10^{-3} at which point the pretreater-effluent will be a satisfactory feed as far as catalyst aging is concerned in the hydrocracking stages. A similar procedure will be followed when the mixed crystalline-amorphous base catalyst of FIG. 3 is used in the hydrocracking stage; only the pertinent numerical value of the tolerable light absorption factor will be different.

The quantitative nature, but not the qualitative nature, of the correlations of FIGS. 2 and 3 vary with the process conditions such as pressure, space velocities, hydrogen circulation rate and conversion levels which were held fixed in generating the data of FIGS. 2 and 3. The quantitative aspects of the correlations also vary from catalyst to catalyst, and for the correlation of FIG. 3, this is shown directly in FIG. 3. For the correlation of FIG. 2, this is shown in Table I in which the performance of two different commercial pretreating-stage catalysts are compared at substantially the same very low degree of aging, at 756° F. and at the fixed process conditions of FIG. 2. The data for catalyst A in Table I are taken from FIG. 2.

While temperature has been used as the controlled process variable in the foregoing illustration of our invention, space velocity, hydrogen circulation and amount of condensed-ring polycyclic aromatics in the feed passed to the pretreating-hydrogenation stage may suitably be used as control variables in analogous ways.

In the processing combination herein described, the feed to the pretreating stage usually has a very much higher organically combined oxygen, nitrogen and sulfur content than that of the subsequent hydrocracking stages. These nitrogen compounds (and ammonia made from them in the pretreater) absorb on the catalyst (probably at acid sites) and deactivate it. Some deactivation of hydrogenation-dehydrogenation sites of the catalyst also occurs by absorption of sulfur and/or nitrogen compounds on them. Therefore, the pretreating stage is run to achieve a relatively low level of hydrocracking, consisting primarily of hydrogenolysis by ring opening of heterocyclic nitrogen, oxygen and sulfur compounds along with limited hydrogenolysis by hydrocracking of hydrocarbons. The temperature necessary to get that kind of desired

conversion with the deactivated catalyst of the pretreating stage is much higher than it would be with the relatively undeactivated or higher activity catalyst of the hydrocracking stage. At the relatively high temperature of the pretreating stage, the hydrogenation activity of the deactivated pretreating catalyst is very great. Thus, hydrogenation of aromatics and unsaturates is the primary hydrocarbon reaction of the pretreating stage, and the data herein presented indicate that it may well be the primary beneficial reaction of that pretreating stage.

In the hydrocracking stage, on the other hand, the concentration of nitrogen and sulfur poisons which deactivate the catalyst is deliberately held low, e.g. at 0.1 to 50 p.p.m. nitrogen in the feed as compared with 100 to 2000 p.p.m. in the pretreating stage. If, therefore, the same catalyst is used in this stage and in the pretreating stage, even the relatively high hydrocarbon conversion desired in the hydrocracking stages will generally be achieved at a lower temperature than that employed for the relatively low conversion desired of the poisoned catalyst in the pretreating stage. In essence, the pretreating stage is operated with a deactivated catalyst at somewhat higher temperatures relative to the temperature of a subsequent hydrocracking stage wherein a catalyst of higher activity is employed.

There are circumstances under which it may be advantageous to operate a single-stage process in which pretreating-hydrogenation and hydrocracking are conducted together at substantially the same process conditions. In the application of this invention to such a process, the amount of polycyclic aromatics in the feed stream, in the recycle liquid stream, or both are monitored as hereinbefore described, and used to control one or more process variables such as temperature, space velocity, hydrogen circulation, amount of polycyclic aromatics in the feed, end point of feed and conversion per pass so that the hydrocracking catalyst will not exceed a desired catalyst aging rate as expressed in degrees F. per day or as catalyst life of at least about 10,000 hours. If the polycyclic aromatics in these streams are monitored by visible and ultraviolet absorption spectroscopy, then the pertinent type of polycyclic aromatics being monitored contain 3 to 7 condensed rings.

Having thus provided a general description of the invention and presented specific examples in support thereof, it is to be understood that no undue restrictions are to be imposed by reason of the specific examples presented except as defined by the claims.

TABLE I.—EFFECT OF CATALYST ON AROMATICS AND NITROGEN CONTENT OF PRETREATING-STAGE EFFLUENT

[1000 p.p.m. N by weight in feed stock]

Operating conditions:		
H_2 circulation rate, s.c.f./bbl.	7,000	
Temperature, ° F.	756	
Space Velocity, LHSV	1.2	
Pressure, p.s.i.g.	2,000	
Designation of pretreating-stage catalyst	A	B
Pretreating-stage effluent:		
Relative concentration of polycyclic aromatics containing 5 to 7 condensed rings as indexed by ultraviolet absorption at 4,480 A., absorption factor $\times 10^3$	10.9	9.0
Organically combined N, p.p.m. by weight	0.25	0.8

We claim:

1. In a process for converting a hydrocarbon feed fraction boiling in the range of 400 to 1100° F. which includes the impurities comprising sulfur, nitrogen and polycyclic condensed ring compounds of three or more rings, said process including the combination of a hydrogenation pretreatment step followed by a hydrocracking step, the improvement in operating on-stream balance between the reaction conditions in said pretreatment step and the concentration of said polycyclic condensed ring compounds in said hydrocracking step, which comprises subjecting said hydrocarbon feed to hydrogenation pretreatment conditions to convert said nitrogen and sulfur impurities to ammonia and hydrogen sulfide and to hydrogenate said polycyclics, controlling the severity of said hydrogenating pretreatment conditions in response to a measured determination of the three to seven condensed ring polycyclic compounds existing in the hydrotreated effluent thereof so that a build-up of said polycyclic compounds will be avoided in the subsequent hydrocracking step and restricting the concentration of polycyclic compounds in said effluent to the hydrocracking step, said polycyclic compounds having light absorption characteristics in the range of 4000 to 5000 angstroms not to exceed 350 p.p.m. and those having light absorption characteristics in the range of 3000 to 4000 angstroms not to exceed about 1000 p.p.m.

2. The method of claim 1 wherein the catalyst in said hydrogenation pretreatment step comprises one or more hydrogenation components dispersed on an amorphous base having cracking activity in the range of 20 to 45 and pores of a size in the range of 30 to 500 angstroms.

3. The method of claim 1 wherein the hydrogenation pretreatment step is maintained at a temperature in the range of 650 to 800° F. employing a hydrogen partial pressure selected from within the range of 1500 to 2500 p.s.i.g.

4. The method of claim 1 wherein the catalyst in said hydrocracking step comprises a crystalline aluminosilicate having a pore size in the range of 6 to 15 angstroms in admixture with an amorphous base cracking component and being promoted with one or more hydrogenating components.

5. The method of claim 1 wherein the hydrocracking step is effected at a temperature selected from within the range of 550 to 750° F. employing a hydrogen partial pressure selected from within the range of 1000 to 2500 p.s.i.g.

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U.S. Cl. X.R.

208—57