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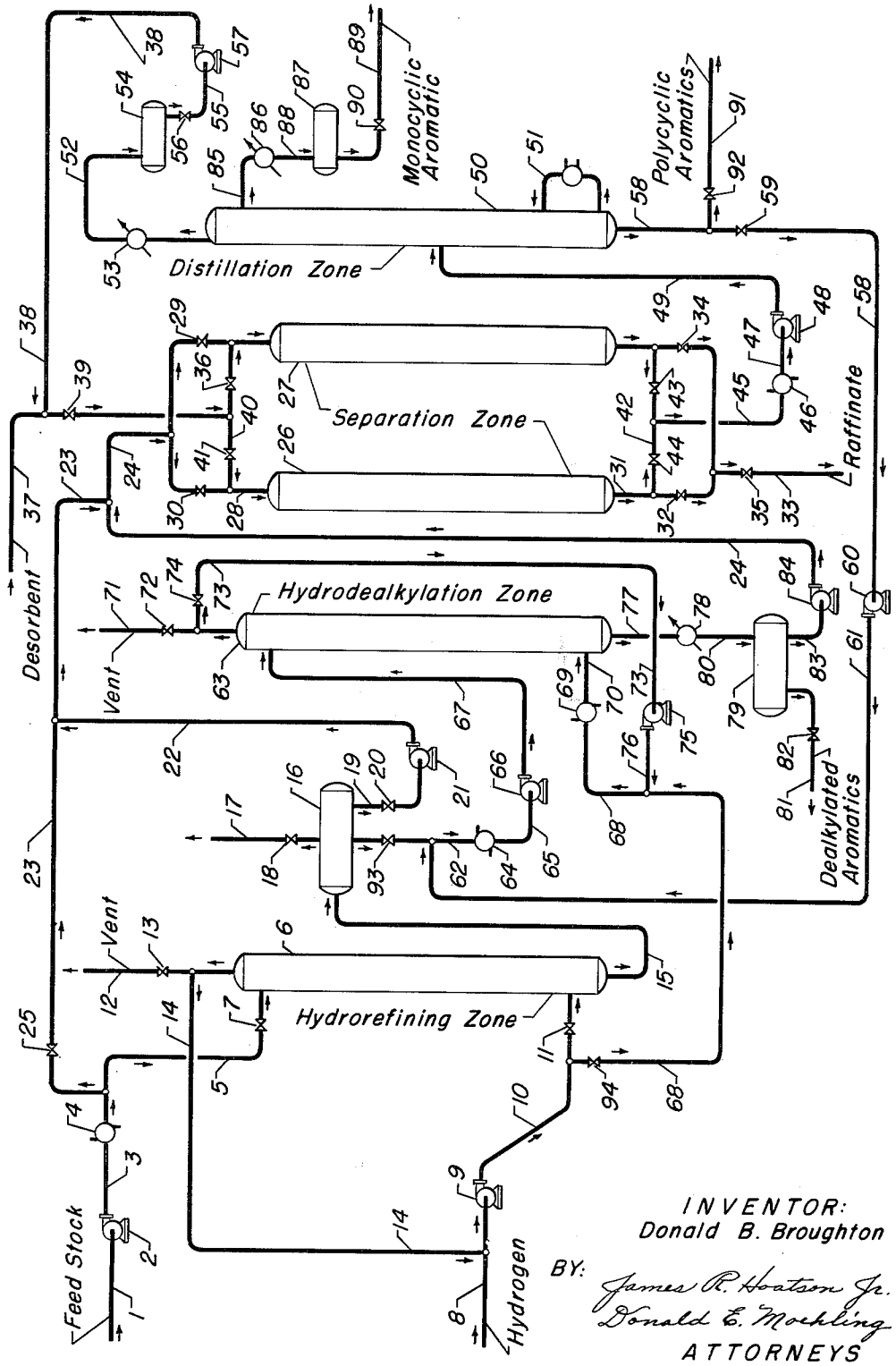

INVENTOR:
Donald B. Broughton

BY: James R. Hoatson Jr.
Donald E. Mochling

ATTORNEYS

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HYDROTREATMENT OF HYDROCARBON STOCKS AND SEPARATION OF AROMATIC COMPONENTS

Donald B. Broughton, Chicago, Ill., assignor to Universal Oil Products Company, Des Plaines, Ill., a corporation of Delaware

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This invention relates to a combination process involving the treatment of alkyl aromatic containing hydrocarbon mixtures in the presence of hydrogen at reaction conditions sufficiently severe to effect the removal of alkyl radicals from the aromatic components and the separation of the resulting aromatic hydrocarbons from the product thereby produced. More specifically, this invention concerns the treatment of hydrocarbon mixtures in the presence of hydrogen to effect the hydrodealkylation of the aromatic components thereof and the recovery via the adsorption technique of the aromatic species present in the mixture, either preceding or following such hydrodealkylation treatment.

The specific and general objectives of the present combination process shall include: increasing the yield of either or both the monocyclic and polycyclic aromatic species of hydrocarbon formed in the hydrodealkylation treatment of middle and upper boiling range hydrocarbon stocks; converting jet fuel boiling range fractions of hydrocarbon fuel oil stocks whereby the luminosity and smoke point of the fraction are reduced and the heat of combustion and the solidification point of the fraction are increased to thereby enhance the burning characteristics and hence the utility of the hydrocarbon mixture for fuel purposes; and increasing the yield of fuel having a given set of quality characteristics in the boiling range of fractions comprising the middle an upper distillates.

In one of its embodiments this invention relates to a multistage process for recovering an aromatic hydrocarbon from a mixture of hydrocarbons containing nuclearly alkyl-substituted homologs of the benzene and polycyclic aromatic series, one stage of the process being a hydrode alkylation reaction in which a hydrocarbon mixture comprising said alkyl-substituted homologs is reacted with hydrogen in the presence of a dealklation catalyst at hydrodealkylation reaction conditions and another of said stages is a separation process wherein the aromatic hydrocarbon-containing mixture selected from the group consisting of: (1) said mixture of alkyl aromatic homologs, and (2) the product of said hydrodealkylation reaction stage comprising a mixture of dealkylated aromatic hydrocarbons is contacted with a solid adsorbent which selectively retains at least one of the aromatic hydrocarbon components of the mixture contacted with said sorbent.

Other generic as well as specific embodiments of the present combination process will be referred to in greater detail in the following further description of the invention.

The present process is especially adapted to the treatment of hydrocarbon mixtures of relatively high boiling point containing alkyl aromatic hydrocarbons of the benzene, naphthalene and the indane, biphenyl, tetralin and acenaphthene series, and in which both the monocyclic and polycyclic components have nuclearly-substituted alkyl substituents. The aromatic components boil within the same general range of temperature as the feed stock and therefore provide a mixture which is generally difficult to separate by fractional distillation or other direct, conventional means. The cyclic hydrocarbon components present in the mixture or formed as a result of one or more of the stages of the present instant process include mono and polyalkyl-substituted benzenes, the naphthalenes and various tricyclic aromatics, as well as bicyclic and tricyclic hydrocarbons containing one or more C_6 rings and one or more 5-membered or 4-membered cycloalkyl or cycloalkenyl rings. The various types of hydrocarbons within the above broad class of aromatics containing one or more rings may be classified according to their compliance to the general formula: C_nH_{2n-j}. Depending upon the number of double bonds in the structure of the aromatic hydrocarbons comprising the feed stock, which thereby determine the value of "*j*," the various cyclic hydrocarbons within this group corresponding to various values of "*j*" may be enumerated as follows:

j=6: Benzenes
j=8: Tetralins and indanes
j=10: Indenes
j=14: Acenaphthenes and biphenyls
j=16: Tricyclic aromatics

Typical sources of hydrocarbon feed stocks containing aromatics and aromatic precursors of the above types are generally the middle and upper distillate fractions of petroleum, boiling for example, from about 400° to about 650° F. at atmospheric pressure, thereby including fractions various referred to in the petroleum refining art as kerosene, gas oil, light and middle cycle oils, diesel fuels, etc. Each fraction, of course, is not mutually exclusive of other classes in the same group, and the initial and end boiling points of the fractions may overlap into other fractions.

The principal object of this invention is the separation of the aromatic components from the nonaromatic hydrocarbons contained in the feed stock for the specific purpose of recovering an aromatic product. For certain other purposes the specific object is the removal of one or both of the mono and polycyclic aromatic components from the hydrocarbon fraction where the objective is the recovery of a substantially aliphatic hydrocarbon product; that is, a product substantially free of aromatic components. The particular sequence of process stages utilized in the present combination process will also depend upon the use to which the product (either the aliphatic raffinate or the aromatic extract) is intended. Thus, the ultimate objective of the process may be the recovery of concentrates of dicyclic aromatics to be utilized as such or further separated into individual components for use as raw materials in a petrochemical process utilizing the dicyclic aromatic as starting material. A particular instance of such selective use is the recovery of naphthalene in a high state of purity for subsequent conversion to phthalic acid.

A particular combination of aromatic products may be prepared in the present combination process which are especially integrated into the combination process, comprising: (1) contacting an aromatic-containing hydrocarbon fraction with an activated silica gel adsorbent to recover both the monocyclic and polycyclic aromatic components on the silica gel, (2) desorbing the mixed aromatics with a desorbent produced in the subsequent hydrodealkylation stage, (3) subjecting the desorption effluent to dehydroalkylation and (4) desorbing the spent adsorbent with the monocyclic aromatic component of the hydrodealkylation stage.

Another end production of a specific method of operating the present combination process is a kerosene or diesel fuel product having improved combustion properties provided by removal of the aromatic components therefrom. Thus, it is known that desel fuels produce smoky exhausts when ignited in a diesel engine because of the presence of aromatic hydrocarbons of either monocylic or polycyclic structure; the present combination process provides a means for removal of such hydrocarbons from a diesel fuel and from kerosene, resulting in

an improved fuel product of substantially greater economic value.

Still another application of the present process wherein the economic value of the product is substantially enhanced is the removal of the aromatic components from jet and rocket fuel fractions (generally boiling in the kerosene and gas oil boiling range), the removal of aromatics resulting in marked improvement in the smoke point, luminometer values and the heats of combustion of these fuels. Thus, the treament of such fractions in the present combination process enables the use of the fuel in a jet or rocket engine without the production of a smoke trail, with greatly reduced exhaust flame and with significantly greater thrust per pound of fuel carried by the vehicle. In the improvement of diesel, jet and rocket fuels, the removal of aromatics is related to an increase in the hydrogen to carbon ratio present in the hydrocarbon components and the average H/C ratio of the hydrocarbon components is increased with the removal of aromatics. Accordingly, the improvement obtained per unit of feed stock to the separation stage of the present combination process will be greater in direct proportion to the quantity of polycyclic aromatics selectively removed from the mixture.

The present process, comprising a combination of at least two stages, including a hydrodealkylation stage and an aromatic separation stage may also be operated for the purpose of preparing specific aromatics utilizable as intermediates for the production of fuels for supersonic aircraft which require fuels of tailor-made composition, principally determined by the necessity of dissipating heat from the combustion zone to the liquid fuel prior to combustion. The vapor pressure requirements for fuels used for supersonic aircraft generally limits the choice of starting materials for such use to hydrocarbon fractions boiling in the kerosene or higher boiling range and in order to provide a fuel capable of absorbing substantial quantities of heat prior to combustion, a fuel having high thermal stability and heat capacity, thermal conductivity and heat of combustion is required. In addition, the fuel, particularly for military aircraft use, must have a low luminometer value. Aircraft flying at supersonic speeds generally must fly in the low temperature regions of the upper atmosphere and the fuel must accordingly have a low freezing point and low viscosity. Although no one type of hydrocarbon satisfies all of the foregoing requirements, generally the monocylic and polycyclic naphthenes have the greatest proportion of desirable properties and are especially adapted for such use. The present combination process provides a means for separating either mixed mono- and polycyclic aromatics or the mono- and polycylic aromatics as individual classes to prepare intermediates for the production of supersonic aircraft fuels via subsequent hydrogenation to their naphthenic analogs.

The process flow and the various alternative methods of operating the present combination process are illustrated in the accompanying diagram which, however, is not intended to illustrate all of the various alternative combinations or specific stages within the broad scope of the present invention. The accompanying diagram, however, does illustrate several alternative process flow arrangements, depending upon the type of feed stock charge to the process and particularly upon the composition of the feed stock. Thus, in the event that the feed stock contains a significant portion of sulfur and/or nitrogen-containing contaminants, the latter are preferably removed or made inactive in the feed stock prior to the hydrodealkylation and/or adsorption stages of the process, since the presence of sulfur and nitrogen-containing compounds in the stream entering the latter stages of the process causes deactivation of the hydrodealkylation catalyst and the preferrential adsorption of these contaminants on the solid absorbent which reduces the capacity of the adsorbent for separation of the desired aromatic product. However, utilizing a feed stock in which the sulfur and nitrogen-containing contaminants are either absent or are present in exceptionally low quantities, the feed stock may either be subjected directly to hydrodealkylation or the aromatic components of the feed stock may be pre-recovered in a preliminary adsorption treatment to provide a concentrate which is thereafter subjected to hydrodealkylation in accordance with one of the alternative flow patterns provided in this invention. In general, the feed stock to the hydrodealkylation stage must contain a relatively high proportion of aromatic components (generally, at least 85+ percent by weight) in order to realize a sufficient degree of conversion to be economically feasible; therefore, a feed stock containing a low cencentration of aromatics is preferably subjected in the initial stage of the present combination process to the adsorption-separation stage in which the alkyl aromatic components are first recovered from the feed stock as an aromatic concentrate and the latter is then subjected to conversion in the hydrodealkylation stage of the present combination process to form the desired dealkylated aromatic product of this invention. Depending upon the choice of sorbent utilized in the adsorption stage of the process flow, the monocylic hydrocarbons may be recovered from the feed stock in admixture with the polycyclic aromatic components (utilizing adsorbents such as silica gel, activated alumina and certain dehydrated zeolitic aluminosilicates) or the later polycycylic aromatics may be selectively recovered from the mono-cyclic components (utilizing an adsorbent such as activated carbon) and separately subjected to hydrodeadlkylation in the present process flow.

Referring to the accompanying diagram, the feed stock containing alkyl aromatic hydrocarbons of mono- and/or polycyclic structure, selected from the middle and upper distillate fractions of petroleum or its conversion products, is charged into the process flow through line **1** from storage by means of pump **2** through line **3** and heater **4** into line **5** from which the hydrocarbon stream may be directed into the several alternative process flow arrangements described above, the temperature to which the feed stock is heated and a pressure to which the feed stock is raised by pump **2** being dependent upon subsequent handling of the feed stock. Most hydrocarbon sources boiling in the middle and upper ranges of petroleum generally contain a sufficient level of sulfur- and nitrogen-containing contaminants to cause the aforementioned catalyst and adsorbent deactivation in the hydrodealkylation and adsorption zones respectively, if not removed from the feed stock prior to such subsequent treatment. Accordingly, the hydrocarbon fraction utilized as feed stock is preferably subjected to a hydrorefining pretreatment to convert the sulfur- and nitrogen-containing compounds into volatile reduction products which may be removed from the hydrocarbon feed stream before the latter is contacted with the solid adsorbent or hydrodealkylation catalyst. In the preferred manner of operating the process, therefore, the raw feed stock is charged by hydrorefining conversion conditions into hydrorefining zone **6** from line **5** through valve **7** which controls the flow rate of hyrocarbons into the hydrorefining zone. As hydrocarbon feed stock flows into reactor **6** at hydrorefining conversion temperature and pressure, hydrogen is simultaneously charged into reactor **6**, preferably into the opposite end of the conversion zone to thereby provide countercurrent flow of the hydrogen relative to the downward flow of feed stock and the fixed bed of hydrorefining catalyst. The hydrogen for this purpose is charged into the process flow through line **8** and pumped by means of compressor **9** through line **10** and at a flow rate controlled by valve **11** into the bottom of reactor **6**. When the feed stock is charged into the hydrorefining zone in vapor phase, the hydrogen gas is preferably in-

troduced concurrently with the feed stock to provide concurrent flow of hydrogen with the hyrocarbon vapors.

The hydrorefining catalyst as maintained within the reactor 6 may be present as a fixed bed of solid particles, or the latter may be circulated in the reaction zone as a moving bed or in a fluidized condition, depending upon whether the hydrorefining conversion is effected in the liquid or gaseous phase.

One of the preferred hydrorefining catalysts for use in zone 6 is one of the platium group metals of Group VIII of the Periodic Table (platinum, palladium, iridium, ruthenium or osmium) composited with a refractory support for the metal, such as alumina, magnesia, zirconia, silica or combinations of these metal oxides, containing from 0.01 to 2 percent by weight of the platinum group metal on the composite. Utilizing a catalyst of this type, the hydrorefining pretreatment may be effected at temperatures of from about 300 to about 1000° F., at pressures of from about 300 to about 1000 lbs./sq. in. and in admixture with sufficient hydrogen to provide a mixture in which the proportion of hydrogen to hydrocarbon (on a mole per mole basis) is from about 0.5:1 to 20:1. Another type of catalyst utilizable in the hydrorefining reaction zone is a composite of an iron group metal of Group VIII of the Periodic Table with the sulfide of a metal selected from the righthand columns of Groups V and VI of the Periodic Tables, such as vanadium, nobium, tantalum, chromium, molybdenum and tungsten, supported on one of the aforementioned refractory metal oxides, such as alumina, zirconia, etc. The preferred iron group metals are nickel and cobalt and the preferred metal sulfides are the thiomolybdates, thiovanadates and the sulfides of niobium and chromium. The preferred refractory metal oxide support is alumina in one of its high surface area forms, such as the eta, gamma or theta variety of alumina. Suitable catalysts contain from about 0.5 to about 4 percent of the iron group metal and from 1 to about 10 percent by weight of the metal selected from Groups V and VI of the Periodic Table. Such catalysts are capable of effecting desulfurization and denitrogenation of the feed stock without saturation of the aromatic double bonds of the hydrocarbons present in the feed stock, even in the presence of high concentrations of hydrogen. Some of the preferred catalyst compositions for use in the hydrorefining zone are nickel and cobalt thiomolybdate (the composite containing about 2.4 percent nickel or cobalt and about 6.4 percent molybdenum) supported on alumina and nickel thiotungstate supported by alumina. The alumina support should not contain more than about a maximum of 2 percent of a basic metal, such as sodium or potassium.

At the indicated hydrorefining reaction conditions the sulfur- and nitrogen-containing organic contaminants present in the feed stock undergo reduction to form ammonia and hydrogen sulfide which may be bled from the top of the hydrorefining reaction zone through line 12 at a rate determined by valve 13. Since the hydrogen is charged into the hydrorefining zone generally in molar proportions exceeding the amount consumed in the reaction, the effluent gas stream removed from the hydrorefining zone contains the excess hydrogen supplied to reactor 6 and the latter excess may be recycled in the process, either directly as recovered from the effluent gas line (with a certain proportion being discharged from the process flow to prevent build-up of impurities in the gas phase) or the hydrogen may be recycled from effluent line 12, preferably after solvent washing to remove the hydrogen sulfide and ammonia from the recycle gas stream. Such solvent washing facilities are not shown on the accompanying diagram, but are of conventional form, inserted in recycle line 14 connecting gas vent line 12 with hydrogen inlet line 8.

The hydrocarbon portion of the hydrorefined product is removed from the bottom of hydrorefining zone (if a downflow operation is employed with a fixed bed of

catalyst in the hydrorefining zone) through line 15 into receiver vessel 16 from which gaseous hydrocarbons dissolved in the liquid product are removed by pressure reduction through line 17 and valve 18. Whether the liquid hydrorefined product is to be subjected to hydrodealkylation directly or first separated into its aromatic and nonaromatic components followed by hydrodealkylation of the recovered aromatics, depends upon the proportion of nonaromatic components in the hydrorefined product. In general the preferred operation comprises separating an aromatic concentrate from the feed stock or the hydrorefined stock and thereafter subjecting the concentrate to hydrodealkylation to produce the desired dealkylated aromatic products. However, with certain feed stocks which contain a high proportion of aromatic components (generally in excess of 75 percent by weight aromatics), generally boiling in the middle and upper distillate ranges, such as a cycle oil recovered as bottoms from the distillation of the product of a hydroreforming reaction, the feed stock may be subjected to hydrodealkylation directly without pre-separation of the aromatic constituents therefrom as an aromatic concentrate to the hydrodealkylation zone. In describing the following preferred type of operation in which an aromatic concentrate is separated from the feed stock prior to dealkylation of the aromatics contained in the feed stock, it is not thereby intended to exclude alternative types of operation, also encompassed within the scope of the present invention, wherein the feed stock is subjected directly to hydrodealkylation, before or after hydrorefining pretreatment. In some instances hydrodealkylation prior to separation may actually be preferable, as for example, when utilizing a feed stock containing from 75 to 95 percent aromatic components as the initial charge stock to the process.

Most sources of aromatic hydrocarbons boiling in the present feed stock range generally contain an appreciable proportion of paraffinic hydrocarbons, such as the C_{12} to C_{28} aliphatic hydrocarbons which are preferably removed from the feed stock prior to hydrodealkylation. In the latter preferred type of process flow the liquid product of the hydrorefining stage from which sulfur- and nitrogen-containing contaminants have been removed during the hydrorefining treatments (or without such prior removal) is withdrawn from receiver vessel 16 through line 19 and valve 20 by means of pump 21 which discharges the hydrocarbons in liquid phase through line 22 into line 23 which in turn connects with line 24 feeding into one of the adsorption towers comprising the present separation zone. In the event that the initial feed stock is to be separated into its aromatic and nonaromatic components without prior hydrorefining pretreatment, valve 7 in line 5 is closed and valve 25 in line 23 is opened, permitting the feed stock to flow directly into line 24. However, although such alternative flow arrangement is contemplated within the scope of this invention, the present feed stocks boiling in the middle and upper distillate boiling ranges generally contain appreciable quantities of sulfur- and nitrogen-containing contaminants which interfere with the separation of the cyclic hydrocarbons in the separation zone and are therefore preferably subjected to the present hydrorefining pretreatment prior to separation of aromatics therefrom in the separation zone. In the event that the feed stock selected for the present process contains little or no sulfur- and/or nitrogen-containing contaminants, such feed stock may be charged directly into either the hydrodealkylation zone (if predominantly aromatic) or into the separation zone without pretreatment in the hydrorefining stage of the process, as described above.

The separation stage of the present combination process is a fixed bed adsorption process utilizing a solid adsorbent of the type capable of selectively adsorbing aromatic hydrocarbons from mixtures of same and aliphatic and/or naphthenic hydrocarbons. In the variation

of the present process in which a polycyclic aromatic hydrocarbon is to be selectively recovered as the desired final product of the present process, the solid adsorbent utilized as packing in the fixed bed separation zone is an adsorbent which preferentially retains the polycyclic aromatic component, distinguishing between polycyclic and monocyclic aromatics, as well as between polycyclic aromatic and aliphatic hydrocarbons. The latter selective adsorbents will be referred to and described more fully hereafter in specifying suitalbe adsorbents for the various processes provided herein.

It has been generally known that solvent extraction techniques have been more widely employed for the separation and recovery of aromatic hydrocarbons from hydrocarbon mixtures than the use of solid adsorbents as the separating agent, generally because liquid-liquid extraction systems have in the past been more readily adapted to continuous processing techniques than solid-liquid adsorption systems, even though certain common solid adsorbents may have greater selectivity and capacity for aromatic hydrocarbons than an equivalent volume of a liquid solvent. The principal reason that adsorption separation has not been more widely accepted is based on the inability of the art to provide a readily operable process on a continuous basis. Thus, in the usual fixed bed adsorption process the flow of feed stock into the bed of adsorbent is interrupted when the adsorptive capacity of the adsorbent is saturated, the removal of adsorbate from the feed stock gradually declining as the adsorbent approaches satiation. Thus, not only is the feed stream discontinuous, but the product stream recovered from the usual fixed bed adsorption process varies in composition continuously throughout the adsorption-desorption cycle. Such fixed bed adsorption processes are difficult to integrate into continuous processes operating upstream and downstream from the adsorption zone and control problems are numerous. Moving bed techniques for adsorbent circulation are generally not feasible with liquid feed stocks, such as are dealt with in the process of the present invention because axial mixing and channeling of liquid through the solid is evident when countercurrent flow of solid adsorbent relative to the liquid phase is attempted. In the present process a continuous flow, liquid-solid adsorption process is provided wherein the aforementioned problems associateed with the usual liquid-solid phase adsorption process are obviated. In one embodiment of the continuous liquid phase process, the separation zone is made up of two fixed beds of solid adsorbent into one of which the feed stream is charged while the other bed undergoes regeneration of the solid adsorbent and from which the adsorbed aromatic components are recovered as a continuous stream in admixture with desorbent. Although such use of the "swing reactor" principle as a means of achieving substantially continuous flow of the liquid stream countercurrent to the solid adsorbent may be utilized and is illustrated herein as a suitable continuous method of adsorptive separation, a more preferred method and apparatus for simulated movement of the solid adsorbent in countercurrent flow relationship to the continuous liquid phase is disclosed in U.S. Patent No. 2,985,589 issued to Donald B. Broughton et al. The adsorption zone comprises one or more fixed beds of solid adsorbent arranged in juxtaposition to provide serial flow or fluid through succeeding beds in series maintained in an adsorption zone containing multiple inlets and outlets, cyclically advanced through the series of fixed beds of the adsorbent continuously or at regular intervals, the liquid feed stock being continuously charged into the fixed beds of solid. The continuous flow arrangement is obtained by the aid of a fluid distribution center in the form of a rotary valve having ports connected to the fluid inlet and outlet points in the adsorption zone, as described in U.S. patent application, Serial No. 805,575, filed April 10, 1959 for D. B. Carson et al.

The solid adsorbent packed into the fixed beds of the separation zone is selected on the basis of the type of separation to be effected in this stage of the combination process. When the ultimate product of the process is to be the entire aromatic content of the feed stock, an adsorbent which is nonselective as to monocyclic and bicyclic aromatics, such as silica gel, activated alumina, certain forms of the class of adsorbents comprising the dehydrated crystalline metal aluminosilicates which are capable of selectively removing aromatic type hydrocarbons from other nonaromatic hydrocarbons and are referred to as zeolitic molecular sieves are utilized as the solid adsorbent in the separation zone. On the other hand, when the aromatic to be recovered is to be selectively restricted to predominantly the polycyclic type, permitting a major proportion of the monocyclic aromatic components to enter the raffinate effluent stream, the solid adsorbent is a material selective for such polycyclic aromatics in the presence of monocyclic, such as activated carbon. Typical forms of the latter activated carbon type of adsorbent include various wood charcoals, especially the charcoals prepared from nutshells, fruit pits and seed pod hulls. One of the preferred adsorbents for use herein is activated cocoanut shell char which has a high degree of selectivity and capacity for polycyclic aromatic hydrocarbons. Other suitable sources of charcoals for the selective recovery of polycyclic aromatics are the carbonized residues of woody plant life, particularly the hard woods, such as maple, oak, teak, etc. Still other suitable charcoals are prepared from petroleum residues, such as the carbonized bottoms recovered from thermally cracked petroleum oils, generally referred to as "petroleum char." The charcoal particles are preferably prepared from materials which when carbonized will yield particles of a size range of from about 10 to about 250 mesh, more preferably from about 15 to about 50 mesh. In order to reduce channeling to a minimum during operation of the separation stage of the process the adsorbent particles are of preferably substantially uniform size, within a size range of about 10 mesh.

Certain other adsorbents which may be utilized as the solid contacting agent in the separation stage of the present process flow which are nonselective with respect to the type of aromatic hydrocarbon in the adsorbent will retain from the mixed hydrocarbon feed stock, include, for example, dehydrated silica gel and dehydrated alumina activated by heating to a temperature not substantially in excess of about 550° C. These adsorbents are prepared by methods widely known in the chemical arts and are preferably of synthetic orgin prepared from the corresponding silica and alumina sols by controlled precipitation from their aqueous gels. Thus, silica gel may be precipitated from an aqueous solution of sodium silicate (water glass) by the controlled addition of a mineral acid thereto until the pH of the solution has been reduced to below 7. Alumina gel may be prepared by precipitating aluminium oxide hydrogel from an aqueous solution of an aluminul salt such as aluminum chloride by the addition to the aqueous solution of an alkali metal or ammonium hydroxide. The gels are filtered, washed with water and dried by heating for several hours at a temperature of from about 110° to about 300° C. The dried solids are activated by heating to a temperature from about 300° to about 550° C. Generally, the gel particles are sifted through screens to separate a product of subtsantially uniformly sized particles.

Still another class of adsorbents utilizable in the separation stage of the present process flow are the synthetic products referred to as molecular sieves comprising adsorbents of the dehydrated metal aluminosilicate type, as described in U.S. Patent 2,882,244, issued to R. M. Milton, and referred to in the foregoing patent as zeolite X, containing pore openings of about 13 Angstrom units.

Other adsorbents of the molecular sieve type include the so-called 10× variety of molecular sieves which, in

common with the 13× variety is also a metal aluminosilicate prepared by the general procedure of mixing an alumina gel with a silica sol (e.g., produced by acidifying an aqueous solution of sodium or potassium aluminum silicate to a pH of about 7), utilizing specified ratios of Al_2O_3/SiO_2, H_2O/SiO_2 and Na_2(or K_2)O/SiO_2. Both types of adsorbents are available commercially from a various manufacturers, such as Linde Air Products Co.

These metal aluminosilicates are the ion exchanged varieties of metal aluminosilicates initially prepared by the formation of a sodium or potassium aluminosilicate wherein the alkali metal derivative is suspended or washed with an aqueous solution of a salt of the metal to be introduced into the zeolite by ion exchange. These metal aluminosilicates are produced in the form of finely divided crystals which are preferably compressed into a matrix of clay to form porous, solid particles which when dried and activated at calcination temperatures of from 150° to about 350° C. are the actual adsorbents utilized in the present separation stage of the process flow. The 10× and 13× varieties of these molecular sieves and the techniques for preparing the same are further described in the foregoing patent references.

The above molecular sieve type of adsorbents, as well as adsorbents selected from the group consisting of silica gel, activated alumina and activated carbon are typically fragile materials which are sensitive to abrasion and reduction to finely divide powders when utilized in moving bed systems for contacting the adsorbent with hydrocarbon feed stock. Thus, under conditions normally causing attrition, such as a moving bed or fluidized method of countercurrently contacting the adsorbent particles with the feed stock in fluid phase the adsorbent would rapidly be reduced to a mass of finely divided particles having excessive flow resistance to the fluid stream. Hence, a system for maintaining the solid adsorbent in a fixed bed while moving the fluid stream through the adsorbent particles, preferably under countercurrent flow conditions, must be provided to realize a reasonable degree of separation of the aromatic components.

The present process flow contemplates two general alternative methods of contacting a fixed mass of solid adsorbent particles with a hydrocarbon stream containing the desired aromatics, the aromatic adsorbate being recovered from the adsorbent by a displacement procedure in which a desorbent stream is contacted with the "spent" adsorbent. For continuous methods of operation, desorption must generally be effected in a separate or different portion of the process flow at essentially the same time that adsorption takes place, either at the same temperature and pressure that the adsorption stage was operated (isothermal operation) or at a higher temperature, depending upon the choice of desorbents, the feed stock and the desired operating conditions. A substantially continuous flow type of process for effecting the alternating adsorption and desorption stages in a pair of adsorbent bed(s) is provided in the so-called "swing reactor" flow arrangement which is illustrated in the accompanying diagram. Thus, the swing reactor principle employs a sorption zone which operates at the same time, but in a separate column, that a fixed bed of adsorbent, maintained in a separate desorption zone, undergoes regeneration. After a fixed period of time (determined by the time required for regeneration of the adsorbent in the desorption zone for recovery of the aromatic adsorbate) the feed stock inlet and desorbent inlets are switched and desorbent enters the zone into which feed stock was charged in the prior cycle, while feed stock enters the zone containing regenerated adsorbent last previously receiving desorbent. Thereafter, the two chambers (that is, the adsorption and desorption zones) are alternatively switched to provide substantially continuous flow of the feed and desorbent streams. A particularly preferred method of continuously and countercurrently contacting the feed stock with a fixed bed of solid adsorbent while simultaneously contacting, also under continuous, countercurrent flow conditions, the desorbent with spent adsorbent containing adsorbed aromatic components is provided in the apparatus and process described in U.S. Patent No. 2,985,589, issued to Donald B. Broughton et al. The latter process and apparatus is especially adapted to the recovery of an aromatic product of high purity, since the adsorption bed is continuously swept free of residual feed stock remaining in the void spaces between the particles of solid adsorbent before the spent adsorbent undergoes desorption. In the swing reactor type of substantially continuous process flow arrangement, however, the feed stock and desorbent residue remaining in each of the adsorption and desorption zones, respectively, enter the stream removed from each of the zones after the function of the zone is switched, thereby contaminating the stream next withdrawn from the zone with such residue of fluid previously charged into the particular zone. For the sake of simplicity of description, however, the present process flow and its principles of operation are adequately described in a swing reactor type of adsorption process which is illustrated in accompanying diagram as the separation zone which comprises two separate beds or columns packed with the solid adsorbent, in one of which (column **26** in the current stage of the process illustrated in the accompanying diagram) adsorption is effected and in the other of which (column **27** at the stage of the process cycle illustrated) the spent adsorbent concurrently undergoes desorption. Both the feed and desorbent streams are shown for illustration purposes entering the top of the adsorption zone **26** and desorption zone **29**, respectively, both streams flowing downwardly through the fixed beds of solid adsorbent, although the separation stage is also operable with either or both the feed and desorbent streams flowing upwardly or downwardly through the fixed bed of solid adsorbent. Under certain conditions it is advantageous for the desorbent to enter at the end of the column opposite to end at which the feed stream entered in the preceding adsorption stage.

The feed stream containing the aromatic components (generally of mixed monocyclic and polycyclic structure, with minor or major proportions of aliphatic and/or naphthenic hydrocarbons) flows through line **24** into line **28** which directs the stream of entering feed stock into either vessel **26** or **27**, depending upon the function of each of the columns. In the description of the accompanying diagram, adsorption is currently effected in vessel **26** and for this purpose valve **29** in line **28** is closed and valve **30** is open, permitting the feed stock mixture to enter the top of vessel **26** and flow downwardly thorugh the fixed bed(s) of solid adsorbent maintained in column **26**. As the feed stream flows downwardly through the adsorbent, the preferentially adsorbed aromatic components of the fed stream displace desorbent retained by the adsorbent particles during the preceding use of vessel **26** as the desorption zone, the preferentially adsorbed aromatic components of the feed stream entering the porous structure of the adsorbent where they are retained via adsorption. Depending upon the particular adsorbent utilized in beds **26** and **27** and the purpose of the present process, the adsorbent solid may be a type which retains all aromatic compounds of both mono- and polycyclic structure, leaving a nonadsorbed raffinate consisting of naphthenic and aliphatic hydrocarbons. Such adsorbents are represented, for example, by silica gel, activated alumina and the above mentioned 10X and 13X molecular sieve zeolites. On the other hand, a selective separation between monocyclic and polycyclic aromatics may be realized by utilizing and adsorbent which is selective for polycyclic aromatics, such as activated carbon of the aforementioned types.

The raffinate consisting of the nonadsorbed components of the feed stock, generally containing a substantial proportion of nonaromatic hydrocarbons, such as paraffins and naphthenes, is removed from the downstream outlet

of adsorption column 26 through line 31 and open valve 32, the stream thereafter entering line 33 which connects with line 31 at the same time that valve 34 is closed to direct the raffinate stream into line 33 for withdrawal from the process at a rate controlled by valve 35.

As aromatics are adsorbed on the solid adsrobent maintained in the current adsorption bed 26, the capacity of the adsorbent gradually decreases until the adsorbent is "spent" or saturated with aromatic adsorbate, as indicated by the sharp rise in the concentration of aromatic adsorbate in the raffinate effluent. At this point the feed stock is diverted into column 27, formerly comprising the desorption stage of the process flow by closing valve 30 and opening valve 29, simultaneously diverting the influent stream of desorbent from column 27 into former adsorption zone 26 by closing valve 36 in line 10.

Desorption which takes place in vessel 27 during the period that adsorption is effected in vessel 26 is the stage of the separation cycle in which the aromatics adsorbed on the solid particles of adsorbent during the adsorption stage are recovered therefrom in the swing reactor cycle of the present process. Although desorption may be effected by raising the temperature of the spent adsorbent to a level at which the aromatic adsorbate is no longer retained by the adsorbent, desorption is preferably effected by separately charging into the desorption zone a liquid or gaseous desorbent capable of displacing adsorbate from the spent solid adsorbent, either by preferential adsorption of the desorbent on the solid adsorbent or by the mechanism based on the Law of Mass Action, whereby the spent adsorbent is surrounded with a molar excess of desorbent, either at the same temperature or at a higher temperature than the adsorption level, causing migration of the adsorbate into the interstitial desorbent fluid surrounding the spent adsorbent particles. The desorbed adsorbate is thereafter recovered from the desorbent comprising the desorption effluent by fractional distillation or other means, depending upon the type of desorbent utilized. In order to effect an appreciable rate of desorption by the Mass Action effect, the desorbent is charged into the desorption zone at a rate sufficient to provide a molar ratio of total desorbent supplied to the desorption zone during the course of the desorption stage to adsorbate initially residing on the adsorbent at least greater than 1:1 up to about 30 to 1 and more preferably a desorbent to adsorbate molar ratio at the beginning of the desorption stage of from about 2:1 to about 10:1.

The preferred desorbents utilizable herein are those compounds which are adsorbed on the solid adsorbent less tenaciously than the aromatic adsorbate component of the feed stock and the desorption of the adsorbate from the adsorbent occurs via the aforementioned Mass Action effect. Further preference is also given desorbents boiling from 10° to 100° F. below the end boiling point of the aromatic adsorbate. Typical desorbents of this type are the mononuclear aromatic hydrocarbons, particularly the lower homologs which are readily recoverable from the adsorbate by fractional distillation. Thus, benezene, toluene, xylene, cumene, ethylbenzene, etc., are especially preferred desorbents utilizable at substantially the same temperature as the adsorption temperature, thereby providing substantially isothermal operation of the overall separation process.

In the case of some feed stocks, however, and when utilizing certain types of desorbents, the rate of desorption may be insufficient to effect complete reactivation of the adsorbent at the same temperature as the adsorption stage and during the same period of adsorption. The inlet temperature of the desorbent stream is thereupon preferably increased to provide a temperature differential between the adsorption and desorption stages from 10° to about 50° C., depending upon other factors. In some instances, particularly when the desorption stage is operated at a temperature relatively elevated with respect to the adsorption stage, the desorbent more preferably is a substantially nonsorbed compound, such as a normal isoparaffinic or naphthenic hydrocarbon individually or in admixture with each other, particularly when the boiling point differential between the desorbent and feed stock is substantial. Typical of the latter type of desorbent is a normal paraffin such as n-hexane, n-octane, n-decane, etc., an isoparaffin such as 2,3-dimethylhexane, 4,5-dimethyldecane, etc., or a mixture of various hydrocarbon types, such as a gasoline boiling range fraction or a straight run petroleum distillate.

During the adsorption of aromatics in vessel 26 of the separation zone desorbent is introduced into the process flow from external sources of supply through line 37 or from internal recycle through line 38, as hereinafter described, the desorbent flowing into the process at a rate controlled by valve 39. The desorbent inlet line 37 connects with line 40 which, in turn, connects at both ends with line 28, flowing during alternate cycles into vessel 26 or vessel 27, depending upon which vessel is currently used as the adsorption or desorption zone of the process cycle. When vessel 27 is the current desorption zone, as illustrated, valve 41 in line 40 is closed and valve 36 is open, thereby admitting desorbent into the top of vessel 27 to flow downwardly therethrough. Since both vessels 26 and 27 contain a substantial void space volume between the solid particles of adsorbent which is capable of holding a considerable volume of feed stock residue after completion of the adsorption stage of the cycle, the latter interstitial fluid is preferably displaced therefrom by desorbent before withdrawal of desorption effluent into the product recovery stages. The point at which the interstitial fluid has been fully replaced by desorbent, indicated by the appearance of desorbent in the desorption zone effluent, is noted by continuous analysis of the desorbent effluent stream. The feed stock residue comprising interstitial fluid is preferably withdrawn from the adsorption column as raffinate effluent, rather than entering the adsorbate product effluent.

The desorption column effluent containing desorbed aromatic component (desorbate), after displacement of the interstitial fluid in column 27, is withdrawn from the downstream outlet of column 27 through line 31 which connects with line 42 into which the desorption effluent flows when valve 34 is closed and valve 43 is open. The flow of desorption effluent (desorbate) from line 31 into desorbate outlet line 45 is effected by closing valve 44 in line 42 connecting with line 31.

The above sequence of valve operations by which the desorption effluent is directed into line 45 for recovery of desorbent and aromatic adsorbate is preferably not initiated until column 27 has been cleared of feed stock residue comprising the interstitial fluid remaining in column 27 then the latter column was utilized as the adsorption zone, as above described. Until the appearance of desorbent in the effluent of column 27, the displaced interstitial fluid is withdrawn through raffinate outlet by leaving valve 34 open as a continuation of the operation of column 27 from the preceding adsorption cycle, while maintaining valve 43 in a closed position to preclude the withdrawal of feed stock residue into the adsorbate product line. The pressure of the fluid phase in line 31 must necessarily, of course, be at least equal to the pressure of the fluid leaving vessel 26 at the same time to prevent back-up flow into vessel 27.

The completion of the desorption stage should preferably occur at substantially the same time as the saturation of the adsorbent in the adsorption column, as indicated by the appearance of adsorbate in the adsorption column effluent. Thus, desorbent is admitted into column 26 by opening valve 41 in line 40 and closing valve 30 in line 28 at substantially the same time that feed stock is charged into column 27 by opening valve 29 and closing valve 36.

The operation of the valves controlling the flow of effluent fluid from columns 26 and 27, however, are preferably

delayed somewhat to permit removal of interstital fluid comprising feed stock from bed **26** (formerly the adsorption bed) before the effluent stream is permitted to enter line **45**. As desorbent flows into the top of column **26** thereafter, valve **32** in line **31** is permitted to remain open until desorbate appears in the effluent of column **26** and valves **34** and **44** are permitted to remain closed until the appearance of raffinate from column **27** and the appearance of desorbent in the effluent stream from column **26**, respectively, the residual feed stock in column **27** thereby flowing into the raffinate product stream outlet (line **33**). Thereafter, valve **32** is closed, valve **44** opened, and valve **43** is closed, directing the desorption effluent (desorbate) into line **45**.

The desorption effluent stream comprising a mixture of aromatic desorbate and desorbent fluid which flows in line **45** is passed through heater **46** which raises the temperature of the desorption zone effluent to a level above the vaporization point of the desorbent. The latter stream leaving heater **46** through line **47** is pumped into line **49** by means of pump **48**, the desorption effluent mixture of aromatic desorbate and desorbent in line **49** being discharged into distillation zone **50**. Additional heat is supplied to the liquid residue accumulating in the lower portion of distillation zone **50** by means of reboiler **51**, continuously vaporizing the more volatile components of the influent stream into the upper plates of zone **50**. When the desorbent is a hydrocarbon more volatile than the feed stock (the preferred type of desorbent), the vapors leaving the top of column **50** through line **52** are substantially pure desorbent which is liquefied in condenser **53** and flows as a liquid condensate into receiver **54**. The recovered desorbent is recycled in the process by withdrawal at a rate controlled by valve **56** from the bottom of receiver **54** through line **55**, the recycle rate being adjusted to maintain the foregoing desorbent to adsorbate ratio in the desorption stage of the process. Pump **57** transfers the recycle desorbent stream from line **55** into line **38** connected to desorbent supply line **37**.

In the event that the separation of the aromatic components from the feed stock is effected prior to the dealkylation stage of the present process flow, in accordance with one of the embodiments of this invention, all of the aromatics recovered from the feed stock in the separation zone boil within the relatively narrow boiling range of the feed stock and may comprise a mixture of both monocyclic and polycyclic varieties which accumulate as a high boiling residue in distillation zone **50**. The resulting bottoms, consisting of both monocyclic and polycyclic aromatics having alkyl side chains attached to the aromatic nuclei when the adsorbent utilized in the separation zone is a non-selective adsorbent such as silica gel, activated alumina or a molecular sieve type metal aluminosilicate and consists of predominantly polycyclic aromatics when the adsorbent utilized in the separation zone is an activated carbon, the aromatics containing alkyl side chains of various carbon atom chain length, are removed from the bottom of column **50** through line **58** and open valve **59** and transferred by means of pump **60** through line **61** into line **62** which feeds the alkyl aromatic extract into hydro-dealkylation zone **63** wherein the mono- and/or polycyclic alkyl aromatics are subjected to hydrodealkylation in the presence of hydrogen to form the desired aromatic product of this invention.

Hydrodealkylation is preferably effected in the presence of a catalyst selected on the basis of its activity in promoting dealkylation of alkyl aromatic hydrocarbons. Suitable catalysts for this purpose are the noble metals of Group VIII of the Periodic Table (platinum, palladium, rhodium, ruthenium, osmium, and iridium) and particularly platinum and palladium, composited with a refractory metal oxide, including typically such oxides as alumina, silica, vanadium oxide, chromium oxide, magnesium oxide, zirconium oxide, molybdenum oxide and others, as well as mixed metal oxides such as alumina-zirconia, silica-alumina, silica-alumina-zirconia, alumina-magnesia, etc. Although the proportion of refractory metal oxide in a mixed metal oxide support is not a critical factor in determining the course of the hydrodealkylation reaction, it is generally preferable that alumina constitutes one of the metal oxide components and that the proportion of alumina in the composite containing the same is maintained at a relatively high level, preferably from 85 to 100 percent of the metal oxide mixture. The proportion of active catalytic component of the composite, that is, the Group VIII noble metal is an important composition variable and in general, the catalyst should contain from 0.01 to 3.0 percent and more preferably from 0.1 to 1 percent by weight of the Group VII noble metal, although the latter proportion is also dependent upon the particular noble metal employed in the catalyst preparation, platinum and palladium being generally required in lower concentrations in the catalyst than other metals of this group.

The catalyst particles are preferably distributed in hydrodealkylation zone **63** in one or more fixed beds supported on perforated trays or other means of distributing the catalyst throughout the length of the reactor. However, depending upon the temperature and pressure conditions maintained in the reaction zone, a fluidized or moving bed system of distributing the catalyst in the feed stock stream may also be employed. In the illustration of the hydrodealkylation process zone in the accompanying diagram, a downflow type of operation, utilized in connection with a fixed bed process, is represented for illustrative purposes only, it being understood that upflow through a fixed bed or the various alternative foregoing moving bed and fluidized bed systems may also be employed in zone **63**. The feed stock entering line **62** flows through heater **64** wherein the temperature of the alkyl aromatic feed stock is increased to the desired hydrodealkylation temperature of from about 1000 to about 1500° F. and more preferably to a temperature within the range of from about 1200 to about 1400° F.

The hydrodealkylation feed stock is thereafter withdrawn from heater **64** through line **65** by means of pump **66** which increases the feed inlet pressure to a level within the range of from about 300 to about 1000 lbs./sq.in. and more preferably to within the range of about 500 to about 900 lbs./sq.in., the hydrocarbon feed stock thereafter entering hydrodealkylation zone **63** through line **67**. Hydrogen is introduced (preferably in countercurrent relationship to the flow of the hydrocarbon feed stock) to provide the desired hydrogen-rich atmosphere in the hydrodealkylation zone. Hydrogen for this purpose and at the pressure utilized in zone **63** is withdrawn from hydrogen supply line **10** at a rate determined by valve **94** through line **68**, heated to the reaction temperature required in hydrodealkylation zone **63** by heat exchange in heater **69** and thereafter charged into zone **63** through line **70**. The unused hydrogen and the short chain hydrocarbons cracked from the alkyl aromatic feed stock during the hydrodealkylation reaction are withdrawn as a mixture from the top of column **63** and may be vented from the process flow through line **71** containing valve **72**, but if desired, valve **72** may be at least partially closed, directing the gas stream into recycle line **73** at a rate controlled by valve **74**. Pump **75** in line **73** returns the hydrogen-containing gas to line **68** through connecting line **76** for recycle purposes. Although countercurrent flow of the hydrogen stream through the catalyst packed reactor is preferably countercurrent (by introduction of the gas stream into the bottom of zone **63**) when feed stock is introduced into the top of the reactor, both feed stocks (hydrocarbon and hydrogen) may be charged concurrently to provide concurrent flow of gas and hydrocarbon phases.

The product of the hydrodealkylation reaction consisting of one or more species of aromatic hydrocarbons of the benzene, indane, tetralin, naphthalene and acenaphthrene types, in admixture or individually, depending

upon the choice of feed stock to the hydrodealkylation zone, is removed from the bottom of reactor **63** through line **77**, cooled in heat exchanger **78** and drained into receiver vessel **79** through line **80**. If the latter product consists of mixed aromatic hydrocarbons, the product may be fractionated by conventional means not illustrated to recover the individual species or the product may be removed directly from the receiver vessel as usable product through line **81** and valve **82**. These hydrocarbons may consist of aromatics free of nuclear alkyl substituents and/or aromatics containing one or more short chain alkyl groups such as methyl and ethyl.

In the alternative process flow of this invention wherein an aromatic concentrate containing at least 85 percent by weight of aromatics is utilized as feed stock and subjected to the preliminary hydrorefining treatment to remove sulfur- and nitrogen-containing impurities prior to hydrodealkylation and prior to separation of the desired aromatics from the fraction, the hydrorefined aromatic concentrate is removed from receiver vessel **16** through line **62** and open valve **93**, thereby charging the feed stream into hydrodealkylation zone **63** which may be operated at relatively more severe temperatures and pressures or for more extended residence times in contact with the catalyst to compensate for the presence of the small amount of nonaromatic diluent. The product of the hydrodealkylation in this flow arrangement is a mixture of dealkylated aromatics, the aliphatic hydrocarbons formed by spliting the alkyl groups from the aromatic components of the charge stock in the form of light aliphatic hydrocarbons are vented from the process flow through line **71** and the heavy aliphatic hydrocarbons present in the initial feed stock to the process which accompanies the desired dealkylated aromatics are removed from the bottom of zone **63** through line **77**. This mixture is removed from receiver vessel **79** through line **83** and transferred by means of pump **84** into line **24** which conveys the hydrocarbon mixture into the separation zone wherein the aliphatic components are removed as reaffinate from the desired dealkylated aromatic product removed from the separation zone through line **45** and discharged into distillation zone **50**. Fractional distillation zone **50** may be operated to produce an intermediate fraction comprising monocyclic aromatic extract, principally benzene and its short chain alkyl-substituted homologs, as well as indane and tetralin, if present, and a separate bottoms fraction comprising one or more varieties of polycyclic aromatics. The intermediate cut is removed from column **50** through line **85**, liquefied in condenser **86** and drained into receiver vessel **87** through line **88**, the product being withdrawn, as required, from receiver **87** through line **89** and valve **90**.

The high boiling bottoms residue in column **50** from which monocyclic aromatics have been reboiled by means of heating coil **51** and comprising one or more species of polycyclic aromatics, depending upon the feed stock initially selected is removed as polycyclic aromatic product from line **58** through line **91** and open valve **92**, valve **59** being closed to direct the polycyclic aromatics into line **91**.

One of the alternative types of flow within the scope of the present invention which provides a method of handling the present feed stocks to form a product of relatively pure aromatic extract. The method is useful in preparing an aromatic concentrate suitable as charge stock to the hydrodealkylation stage of the process from a hydrocarbon mixture (such as a petroleum fraction or the product of an aromatic producing conversion reaction such as a fraction of a hydroforming reaction product) which may also contain nitrogen- and sulfur-containing contaminants. The feed stock admitted into the process flow through line **1** is pumped directly into line **23** through open valve **25** by closing valve **7**, the feed stock thereafter entering line **24** which feeds into the separation zone. The adsorbent utilized in the separation zone is a solid which selectively extracts one or more types of aromatic components from the mixed hydrocarbons in the feed stock, in addition to the relatively polar sulfur- and nitrogen-containing compounds present in the feed stock. The aromatic desorbate product, recovered from the desorbent as bottoms in distillation column **50** is transferred in toto by means of pump **60** into line **5** between valve **7** and hydrorefining reactor **6**, being heated (by means not illustrated on the accompanying diagram) to the hydrorefining reaction conditions prior to entry into zone **6**. This alternative flow enables the recovery of an aromatic concentrate from a dilute initial feed stock, thereby reducing the volume of feed stock which the hydrorefining zone is required to handle.

The present invention is further illustrated with respect to several of its specific embodiments in the following examples which are introduced for illustrative purposes only without necessarily limiting the generally broad scope of the invention in accordance therewith.

EXAMPLE I

A light cycle oil hydrocarbon fraction suitable as a diesel fuel, having a bromine number index of 6.4 and containing 1.24 percent by weight of total sulfur, 200 p.p.m. of total nitrogen and having other characteristics set forth in the following Table I:

Table I.—Properties of light cycle oil charge stock

° API gravity	27.9
Boiling point range,[1] ° F.:	
Initial B.P.	403
50% over	500
End B.P.	595
Smoke point, mm.	11.0
Luminometer No.	33.1
Diesel index	30.1
Composition, volume percent:	
Saturates+olefins	52.4
Aromatics[2]	47.6
j=6	17.9
j=8	8.3
j=10	1.7
j=12	13.6
j=14	4.4
j=16	1.0
j=18	0.7

[1] By standard ASTM procedure.
[2] The value of j is equal to its value in the following emperical formula : C_nH_{2n-j}.

This fraction is subjected to a preliminary hydrorefining treatment by charging the feed stock at a temperature of about 900° F. and at a pressure of 600 lbs./sq. in. into a fixed bed hydrorefining reactor packed with a catalyst consisting essentially of a composite of nickel (2.4 weight percent) and molybdenum (6.4 weight percent) on a high surface area alumina containing less than 1 percent sodium. The feed stock was charged into the hydrorefining reactor with a mixture of fresh hydrogen (100 s.c.f./bbl. of feed stock) and recycle gas to form a mixture in which the hydrogen concentration is about 70 percent, the charge stock being fed into the reactor at a hydrogen presure of 200 lbs./in.^{2} and at a liquid hourly space velocity (volumes of liquid per volume of catalyst per hour) of about 3. The product contained approximately 29 p.p.m. of sulfur and 63 p.p.m. of nitrogen. The composition of the product was unchanged insofar as aromatic and paraffin content is concerned.

The liquid fraction of the resulting product was then charged into a separation column of the multiple, serially interconnected fixed bed type described in U.S. Patent No. 2,985,589 containing 24 fixed beds of solid absorbent consisting of activated silica gel particles of 20–30 mesh in size. The solid adsorbent was effectively moved through the feed stock in simulated countercurrent flow relationship to the feed stock which flowed upwardly

through the fixed beds by moving the fluid inlets and outlets to each bed in the column equidistantly and cyclically through the series of beds with the aid of a fluid distribution center comprising a rotary valve with a number of inlet and outlet ports corresponding to the number of fixed beds in the separation column, the apparatus and method being described in application Serial No. 805,575, filed April 10, 1959, now Patent No. 3,040,777, for D. B. Carson et al.

The desorbent utilized in the separation stage to displace aromatics from the adsorbent was benzene charged at a desorbent to adsorbate rate of 10 to 1 moles/mole.

The raffinate (nonaromatic, nonextracted portion) and extract fractions recovered from the hydrorefined product are characterized in the following Table II:

Table II.—Properties of raffinate and extract products recovered by adsorption with activated silica

	Charge (Hydrorefined Product)	Extract	Raffinate
Gravity, °API	30.2	13.2	39.4
Boiling Point Range,[1] ° F.:			
Initial	415	425	409
50% Over	493	530	496
End Point	552	635	637
Total Sulfur, p.p.m.	310	2.31	97
Total Nitrogen, p.p.m.	103		
Composition, Volume Percent:			
Paraffins	34.5	0.8	67.1
Naphthenes	20.7	0.5	27.1
Aromatics (Vol. Percent, Total)	42.1	95.0	3.3
$j=6$	14.3		29.1
$j=8$	4.9		38.5
$j=10$	1.8		6.2
$j=12$	14.8		5.2
$j=14$	4.6		10.7
$j=16$	1.1		4.5
$j=18$	0.4		0.8

[1] By ASTM procedure.

The above extract fraction separated by adsorption on an activated silica gel adsorbent, 95 percent of which is aromatic was charged at a temperature of 1250° F. together with a concurrent stream of hydrogen (88% by weight) at a pressure of 300 p.s.i.g. and at a liquid hourly space velocity of 3.0 into a fixed bed hydrodealkylation reactor packed with a catalyst in the form of ⅛" diameter spheres containing 0.30 percent by weight of platinum supported on an alumina base. The effluent product was cooled to condense the liquid products from the noncondensable gases which consisted principally of hydrogen and C_1 to C_5 hydrocarbons. A major proportion of the liquefied hydrocarbon product was consisted of benzene and naphthalene (about 83 percent), formed by the hydrodealkylation of their monoalkyl and polyalkyl derivatives present in the feed stock and having boiling points in the feed stock boiling range. The remaining aromatic components of the liquid product were the methyl and ethyl (predominantly mono-nuclearly substituted) derivatives of benzene and naphthalene.

EXAMPLE II

In the following run, the alkylnaphthalene aromatic components and most of the nitrogen and sulfur-containing components present in a light cycle oil recovered from a Mid-Continent crude oil were selectively extracted with only minor quantities of monocyclic aromatics in the extract. The starting feed stock to the process has the following properties indicated in Table III, below:

Table III.—Light cycle oil properties used as charge stock

Specific gravity, @ 60° F.	0.8785
Total sulfur, wt. p.p.m.[1]	555/585
Total nitrogen, p.p.m. by wt.	142
Pour point, ° F.	−20
Boiling point range, ° F.:	
Initial	410
10% over	430
50% over	486
End point	549
Analysis[2], wt. percent of aromatic and olefin portion:	
Alkyl benzenes	20.86
Indane+tetralins	27.87
Indenes	1.76
Alkylnaphthalenes	44.70
Acenaphthenes+biphenyls	4.29
Dehydroanthracenes	0.39
Obenanthrenes	0.12
Analysis,[2] wt. percent of paraffins and naphthene portion:	
Paraffins	62
Monocyclic naphthenes	22
Polycyclic naphthenes	16

[1] By Wickbold method.
[2] By mass spectrographic analysis.

The above light cycle oil was charged into the multiple bed (containing 24 beds), simulated moving bed, continuous countercurrent flow unit specified in Example I, above, each bed being packed with 23 grams of 30–50 mesh activated carbon (type BPL, Pittsburgh Chemical Co.). The feed stock was charged into the column at 300° F. and at a pressure of 150 p.s.i.g. The adsorbed aromatics were desorbed from the activated carbon with benzene, utilizing a flow rate of desorbent to adsorbate of 10 to 1. The following extract and raffinate products (Table IV) having the indicated properties were recovered in their indicated yields and purities.

Table IV.—Products recovered by adsorption on activated carbon

	Extract	Raffinate
Recoveries, Liquid Volume Percent:		
Aromatics, Total	6.4	35.6
Nonaromatics	3.2	96.8
Types—		
$j=6$	16.3	83.7
$j=12$	99.3	0.7
$j=12+$	98.3	1.7
Total Sulfur, Wt. Percent	95.3	4.7
Total Nitrogen, Wt. Percent	97.3	2.3
Adsorbate Analysis, Wt. Percent:		
$j=6$	4.73	
$j=8$	19.27	
$j=10$	2.35	
$j=12$	66.50	
$j=14$	6.38	
$j=16$	.65	
$j=18$	.13	

The above extract fraction containing predominantly alkyl polycyclic aromatics selectively extracted from the light cycle oil is subjected to a hydrorefining treatment utilizing the hydrorefining catalyst and conditions specified for the operation in Example I, above, the severity of the treatment being designed to eliminate nitrogen and sulfur contaminants without affecting the composition or identity of the aromatic components. The hydrorefined product contained essentially the same aromatic components in substantially the same proportion as the feed stock, but the sulfur and nitrogen contents were reduced from 0.076 weight percent (76,000 p.p.m.) total sulfur in the feed to the hydrorefining unit to 66 p.p.m. of sulfur; the total nitrogen content was reduced from 142 p.p.m. in the feed stock to less than 5 p.p.m. in the hydrorefined product.

The treated extract, now substantially free of sulfur and nitrogen contaminants was then charged into a hydrodealkylation reactor at 1200° F., 500 p.s.i.g. pressure and at a liquid hourly space velocity of 2.5 volumes of feed stock per volume of catalyst per hour. Hydrogen at the above pressure and temperature was simultaneously charged at a 12 to 1 molar ratio into the bottom of the hydrodealkylation reactor and the reactor effluent was taken overhead through a water-cooled condenser to remove condensable vapors and then removed from the process. The catalyst packing in the reactor was a palladium-alumina-silica composite in the form of ⅛ x ⅛ inch

pills containing 0.35 percent by weight of palladium impregnated on a support consisting of 88% SiO_2 and 12% Al_2O_3. The liquid product was recovered in a yield of 88 percent by weight of the charge stock, the alkyl group removed from the aromatic nuclei appearing as methane in the overhead noncondensable gas. The following Table V specifies the product distribution:

Table V

Aromatics, wt. percent:	
j=6 (benzene)	1.8
j=8 (tetralin and indane)	2.6
j=10 (indene)	1.4
j=12 (naphthalene)	82.1
j=14 (acenaphthene+biphenyl)	8.6
j=16 and 18 (anthracenes)	5.5

I claim as my invention:

1. The process for recovering an aromatic hydrocarbon from a mixture of hydrocarbons containing nuclearly alkyl-substituted homologs of the benzene and polycyclic aromatic series together with sulfur- and nitrogen-containing impurities, which comprises initially subjecting said mixture to a hydrorefining treatment in the presence of hydrogen and at hydrorefining reaction conditions whereby the sulfur- and nitrogen-containing compounds present in the feed mixture are converted to volatile nitrogen- and sulfur-containing compounds and the nitrogen and sulfur content of the normally liquid portion of the feed stock is substantially reduced, thereafter contacting the resulting hydrorefined product with a solid adsorbent under conditions whereby the alkyl aromatic hydrocarbon components present in the hydrorefined product are selectively recovered from the nonaromatic components of the mixture and subjecting the recovered alkyl aromatic hydrocarbons to hydrodealkylation in the presence of hydrogen and a hydrodealkylation catalyst at a temperature and pressure sufficient to remove the nuclear alkyl substituents from the alkyl aromatic components of the feed stock to the hydrodealkylation reaction.

2. The process of claim 1 further characterized in that said hydrodealkylation catalyst comprises a noble metal of Group VIII of the Periodic Table composited with a refractory metal oxide.

3. The process of claim 2 further characterized in that said metalis platinum and the metal oxide is alumina.

4. The process of claim 1 further characterized in that the hydrodealkylation reaction is effected at a temperature of from about 1000° to about 1500° F. and at a hydrogen pressure of from about 300 to about 1000 lbs./sq. in.

5. The process of claim 1 further characterized in that said solid adsorbent is activated carbon and said alkyl aromatic homologs are predominantly composed of alkyl-substituted polycyclic aromatic hydrocarbons.

6. The process of claim 1 further characterized in that said solid adsorbent is selected from the group consisting of activated silica gel, activated alumina and a dehydrated, zeolitic metal alumino-silicate adsorbent capable of adsorptively retaining aromatic hydrocarbons of both mono- and polycyclic structure.

7. The process of claim 1 further characterized in that said hydrorefining treatment is effected in the presence of a nickel-containing catalyst.

8. A combination process for the production of an aromatic hydrocarbon from a hydrocarbon mixture containing monocyclic and polycyclic alkyl aromatic hydrocarbons boiling in the range of from about 400° to about 650° F. together with sulfur- and nitrogen-containing compounds, which comprises subjecting said mixture to a preliminary hydrorefining treatment in the presence of hydrogen at desulfurization and denitrogenation reaction conditions, thereafter contacting the resultant hydrorefined product of reduced sulfur and nitrogen content with activated silica gel capable of adsorbing an aromatic hydrocarbon in an adsorption zone at aromatic adsorption conditions, desorbing adsorbate comprising both the monocyclic and polycyclic aromatic components in the mixture with a monocyclic aromatic hydrocarbon produced in the subsequent hydrodealkylation reaction stage to form thereby a desorption effluent comprising monocyclic and polycyclic feed stock aromatic hydrocarbon adsorbate and monocyclic aromatic hydrocarbon desorbent, subjecting said desorption effluent to hydrodealkylation in the presence of hydrogen and a hydrodealkylation catalyst, fractionating the resulting product mixture of the hydrodealkylation reaction stage to separate a polycyclic aromatic hydrocarbon product from a more volatile fraction comprising a substantially dealkylated monocyclic aromatic hydrocarbon and charging a desorbent quantity of said more volatile fraction into said adsorption zone as said desorbent.

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ALPHONSO D. SULLIVAN, *Primary Examiner.*