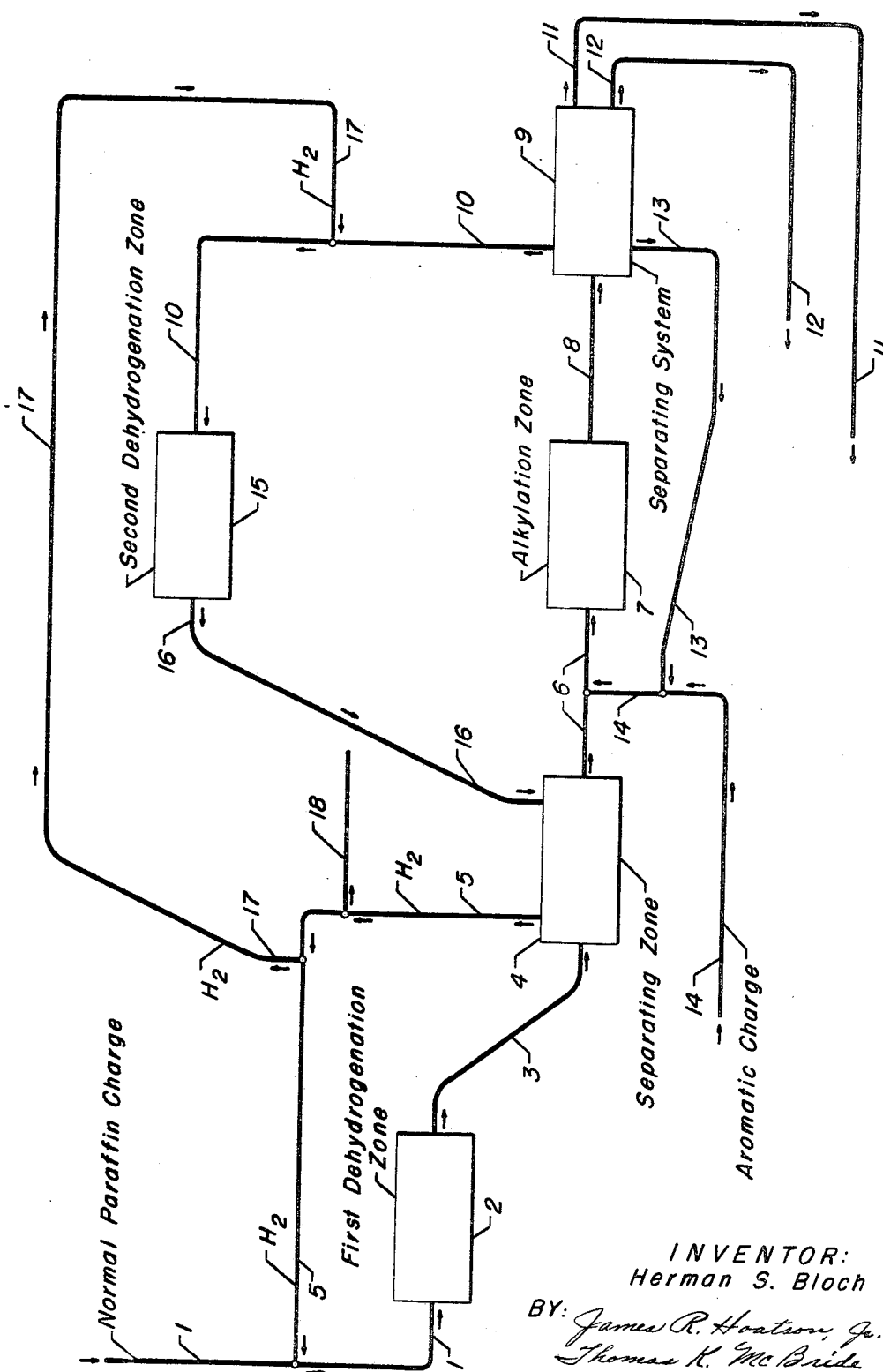


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CATALYTIC DEHYDROGENATION OF CONTAMINATED
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CATALYTIC DEHYDROGENATION OF CONTAMINATED NORMAL PARAFFIN HYDROCARBONS**Herman S. Bloch, Skokie, Ill., assignor to Universal Oil Products Company, Des Plaines, Ill., a corporation of Delaware**

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ABSTRACT OF THE DISCLOSURE

A hydrocarbon stream containing normal paraffins, having about 6 to 20 carbon atoms, and a catalyst-deactivating cyclic contaminant is selectively dehydrogenated to form normal mono-olefins having the same number of carbon atoms as the normal paraffins. Catalyst utilized contains a platinum group component, an alkali component, and an alumina component. Process involves the steps of: dehydrogenation of input hydrocarbon stream, recovery of unreacted normal paraffins, separate dehydrogenation of the recovered paraffins, and continuous passage of the product stream from the last dehydrogenation step to the paraffin recovery step, thereby recycling the unreacted normal paraffins to extinction. Key feature of the resulting process involves charging fresh feed exclusively to the first dehydrogenation step and charging the recovered unreacted normal paraffins exclusively to the second dehydrogenation step, thereby facilitating control of the catalyst-deactivation produced by the cyclic contaminant and improving selectivity and stability of the over-all process.

The subject of the present invention is an improved process for the preparation of normal mono-olefins having about 6 to about 20 carbon atoms from a hydrocarbon stream containing the corresponding normal paraffins and a catalyst-deactivating cyclic contaminant. More specifically, the present invention comprises a method of improving the performance of a catalytic dehydrogenation process which operates on an input stream containing long-chain normal paraffins and a minor amount of a catalyst deactivating cyclic impurity in order to produce long-chain normal mono-olefins without producing any substantial quantity of undesired side products and with ultimate complete conversion of the normal paraffins contained in the input stream.

Although extensive work has been done in the general area of production of mono-olefins from paraffins, the chief effort in the past has been primarily concentrated on lower molecular weight paraffins (i.e. paraffins having 2 to 6 carbon atoms). This concentration of effort was basically caused by the ready availability of large quantities of these paraffins and, probably, by the extensive demand for the product olefins as chemical building-blocks. Recently, attention within the chemical and petroleum industry has been focused upon the problem of acquiring longer chain mono-olefins. In particular, a substantial demand has been established for normal mono-olefins having 6 to 20 carbon atoms. As might be expected, this demand is primarily a consequence of the growing commercial importance of the products that can be synthesized from these normal mono-olefins. For example, derivatives of normal mono-olefins have become of substantial importance to the detergent industry because these normal mono-olefins can be used to alkylate an alkylatable aromatic, such as benzene, and the resulting arylalkane can be transformed into a wide variety of biodegradable detergents such as the alkylaryl sulfonate (anionic) type of detergent which is most widely used for household, commercial and industrial purposes. Another type of de-

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tergent produced from this arylalkane is alkylaryl-polyoxyalkylated amine. Still another large class of detergents produced from these normal mono-olefins are the oxyalkylated phenol derivatives in which the alkyl-phenol base is prepared by alkylation of phenol.

Other uses of the long-chain mono-olefins include: direct sulfation to form biodegradable alkylsulfates of the type $R-OSO_3Na$; direct sulfonation with $NaHSO_3$ to make biodegradable sulfonates of the type RSO_3Na ; hydration to alcohols which are used to produce plasticizers or synthetic lube oils; hydration to alcohols followed by dehydrogenation to form ketones which can be used in the manufacture of secondary amines by reductive alkylation; ester formation by direct reaction with acids in the presence of a catalyst such as BF_3 -etherate; and in the preparation of di-long chain alkylbenzenes, of which the heavy metal sulfonate salts are prime lube oil detergents.

Responsive to this demand for these normal mono-olefins, the art has developed a number of alternative methods to produce them in commercial quantities. One method, that has attracted a great deal of attention, involves the selective dehydrogenation of a normal paraffin-containing stream by contacting it and hydrogen with a non-acid, alumina-supported, platinum metal-containing catalyst. The principal feature that distinguishes this method from previous attempts at the solution of the problem of direct dehydrogenation of long-chain normal paraffins, involves the capability of this catalyst to sustain a high level of selectivity for the production of the desired normal mono-olefins with the complementary capability to suppress undesired side reactions such as skeletal isomerization, secondary dehydrogenation, dehydrocyclization, polymerization, cracking, etc. The term "selectivity" is used herein to measure the weight percent of the conversion products from the dehydrogenation reaction that are the desired long-chain normal mono-olefins; for example, if 10 wt. percent of a feed stream is converted in one pass through the dehydrogenation zone and about 8 wt. percent of the feed stream is converted to normal mono-olefins, the selectivity is 80%. Likewise, for a process operated to obtain 100% conversion of the input stream, the selectivity is measured by the weight percent of the input stream that is recovered as normal mono-olefins.

In order to further enhance this selectivity feature of this dehydrogenation method, it is ordinarily conducted at severity levels resulting in a weight percent conversion per pass through the dehydrogenation step in the range of about 5 to 20 wt. percent. This last limitation is a consequence of the observed decrease in selectivity levels, attainable in this method, as a direct function of severity levels utilized: that is, high conversions require high severity levels which in turn substantially degrade selectivity. Hence, this dehydrogenation method must be operated with a low conversion per pass, and because of this, the economics of the resultant process dictate that the unreacted normal paraffins present in the output stream from the dehydrogenation step be recovered and recycled to extinction. Accordingly, a preferred process for the preparation of long-chain normal mono-olefins from normal paraffins involves the steps of: (1) selective dehydrogenation using a catalyst containing a platinum group component, an alkali component, and an alumina component; (2) separation of products, and (3) recycle of unreacted normal paraffins.

It is to be emphasized that the retention of this high selectivity feature of this preferred process is a critical condition for its stable operation. This is true because the unreacted normal paraffins that are recycled are separated in a recovery system which does not have the capability to distinguish between types of hydrocarbons in a given boiling range—for example, a typical recovery system uses distillation means to separate the unreacted

normal paraffins from a derivative of the normal mono-olefins. Accordingly, any side products of the dehydrogenation step that boil within the boiling range of the normal paraffins accumulate in this recycle paraffin stream. This contamination of the recycle paraffin stream with side products of the dehydrogenation reaction such as isoparaffins, alkylaromatics, etc. leads to several significant adverse effects: namely, the quality of the normal mono-olefins, or derivatives thereof, recovered from the process is degraded by the presence of olefin derivatives of these isoparaffins, and the stability of the process is upset by the presence of these isoparaffins and alkylaromatics in the recycle stream because high severity levels in the dehydrogenation step are necessary to sustain the same conversion level. This last effect is caused by the refractory nature of certain isoparaffins and alkylaromatics relative to normal paraffin hydrocarbons at conditions utilized in the dehydrogenation step, leading to high severity levels which further degrade selectivity and activity of the dehydrogenation catalyst. From these considerations, it is evident that a decrease in selectivity of the catalyst system employed in the dehydrogenation zone will ultimately accelerate the deactivation of the system because of the rapid amplification of this decrease in selectivity through feed-back to the dehydrogenation zone of refractory non-normals contained in the paraffin recycle stream.

The problem addressed by the present invention stems from the commercial necessity of charging to this preferred process a hydrocarbon stream that contains minor amounts of catalyst-deactivating contaminants. Typically, this situation is encountered where the feed stream to the dehydrogenation process is derived from a hydrocarbon distillate containing both normal and non-normal hydrocarbons in the desired boiling range, by a selective extraction process using a bed of molecular sieves of the proper pore size. In this type of separation operation there is a trade-off between extract product purity and yield which normally is resolved by allowing a minor amount of non-normal components to be included in the extract stream from the system. I have now found that the non-normal portion of the substantially pure normal paraffin-containing stream from this type of separation process can contain cyclic compounds such as alkyl-naphthenes, alkylaromatics, bi-cyclic naphthenes, or alkylindanes, which have the capability to deactivate the dehydrogenation catalyst used in the dehydrogenation step of this preferred process. Regardless of how these contaminants get into the feed stream for the dehydrogenation process, it is clear that their presence can rapidly jeopardize the stability and product quality of this preferred process because the catalyst deactivation produced thereby is ordinarily compensated for by raising the severity in the dehydrogenation step, thereby leading to a decrease in selectivity and accelerated deactivation of the catalyst as explained above. Accordingly, for this preferred process a small amount of catalyst deactivation can severely affect process stability in view of the multiplying effect of the recycle stream.

It might be thought that this hydrocarbon feed stream can be easily treated by conventional means to remove these contaminants; but such is not the case for the reason that these conventional treating means typically involve subjecting the hydrocarbon stream to conditions which involve a substantial risk of degrading the normal paraffin content of this feed stream. Hence, the problem is to pretreat the feed stream to remove these contaminants without generating any substantial quantity of non-normal hydrocarbons, and I have now found such a pretreatment procedure. In essence, my method comprises using a portion of the selective dehydrogenation catalyst in a first dehydrogenation step designed to remove the contaminants from the fresh feed stock coupled with a second dehydrogenation step using this preferred type of catalyst which operates only on recovered normal paraffin

hydrocarbons, thus isolating the adverse effects of the fresh feed contaminants from the unreacted normal paraffin recycle loop wherein any decay in selectivity tends to be rapidly amplified.

It is, accordingly, an object of the present invention to provide an improved process for the selective catalytic dehydrogenation of a hydrocarbon stream containing normal paraffin hydrocarbons and a catalyst-deactivating cyclic contaminant. Another object relates to a selective catalytic dehydrogenation process which uses a non-acid, alumina-supported, platinum metal-containing catalyst to dehydrogenate a hydrocarbon feed stream containing normal paraffin hydrocarbons and a catalyst-deactivating cyclic contaminant, in which process unreacted normal paraffins are recovered and recycled to extinction, the object being to improve the selectivity and stability of the over-all process. Another object relates to a process of the type described above, the object being to provide a means for removal of cyclic contaminants from such a hydrocarbon feed stream without producing any substantial amount of non-normal components. Still another object is to control the principal cause of deactivation for such a process and to facilitate catalyst regeneration or replacement operations by providing a point of major catalyst deactivation in the process.

In one embodiment, the present invention comprises a catalytic process for dehydrogenating a hydrocarbon stream containing normal paraffin hydrocarbons having about 6 to about 20 carbon atoms, and a catalyst-deactivating cyclic contaminant. The process comprises the steps of: (a) contacting, in a first dehydrogenation zone, the hydrocarbon stream and hydrogen with a first catalyst containing a platinum group component, an alkali component, and an alumina component, at dehydrogenation conditions sufficient to form a first effluent stream containing normal mono-olefins having the same number of carbon atoms as said normal paraffin hydrocarbons, hydrogen, and unreacted normal paraffin hydrocarbons; (b) withdrawing the first effluent stream from this zone and separating hydrogen therefrom to obtain a first mixture of the normal mono-olefins and unreacted normal paraffin hydrocarbon; (c) removing the normal mono-olefins from the first mixture to form a stream containing unreacted normal paraffin hydrocarbons; (d) contacting in a second dehydrogenation zone said last stream and hydrogen with a second dehydrogenation catalyst having a platinum group component, an alkali component, and an alumina component at conditions selected to produce a second effluent stream containing the normal mono-olefins, hydrogen and unreacted normal paraffin hydrocarbons; and, (e) withdrawing this second effluent stream from the second zone, separating hydrogen therefrom to form a second mixture of the normal mono-olefin and unreacted normal paraffin and passing this second mixture to the removing step.

In the second embodiment, the present invention encompasses a process of the type described above wherein the removing step comprises: contacting the first mixture and an alkylatable aromatic with an alkylation catalyst at alkylation conditions; withdrawing an effluent stream from contact with the alkylation catalyst; and separating from this last effluent stream, the stream containing the unreacted normal paraffin hydrocarbons with accompanying recovery of a fraction containing aryl-substituted normal paraffins.

In another embodiment, the present invention relates to a process as described in the first embodiment above, wherein the removing step comprises: contacting the first mixture and the second mixture with an adsorbent material having a high selectivity for the mono-olefins, and withdrawing from contact with the adsorbent material the stream containing the unreacted normal paraffin hydrocarbons.

Other embodiments and objects of the present invention encompass further details about: the hydrocarbon streams

that can be charged thereto, the types of catalysts that can be used in the dehydrogenation steps thereof, the process conditions used in each step thereof, the mechanics of the conversion, separation, and product recovery steps employed therein, etc. These embodiments and objects will become evident from the following detailed discussion of each of these facets of the present invention.

A feature of the present invention is the use of different dehydrogenation steps for the fresh hydrocarbon stream and for the recovered unreacted normal paraffin-containing stream. This contrasts with the usual recycle operation of the prior art wherein there is a single dehydrogenation step with recycle of the unreacted normal paraffins directly thereto. As was pointed out hereinbefore, the idea for this two-step process is grounded in a finding that most of the hydrocarbons that are suitable charge stocks for the type of process of concern here contain contaminants that are a major cause of catalyst deactivation. An advantage of the two-step operation is that it concentrates the deactivation in the first step of the process and because the conversion in both steps is generally low, usually not over 10 to 20% per pass, the amount of catalyst utilized in the first step is much smaller than in the second step thereby facilitating regeneration of the catalyst in the first step (as by the utilization of a pair of swing reactors), or replacement of the catalyst if such is desired. Another advantage of this process is that it permits the selection of operating conditions and catalysts for the two-dehydrogenation steps to be based on the function of each step: the function of the first step being the removal of the catalyst deactivating contaminant without generating any non-normal components, the function of the second step being the selective catalytic dehydrogenation of the normal paraffins. Yet another advantage is the elimination of the major cause of catalyst deactivation from the second dehydrogenation step where 80 to 90% of the dehydrogenation typically takes place, thereby greatly increasing the stability of this second step which is obviously reflected in greater selectivity and stability for the over-all process.

The hydrocarbon stream that can be charged to the process of the present invention contains normal paraffin hydrocarbons having at least 6 carbon atoms and especially 9 to about 20 carbon atoms. Representative members of this class are: hexane, heptane, nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane, octadecane, nonadecane, eicosane, and mixtures thereof. Hydrocarbon streams containing normal paraffins of 10 to 15 carbon atoms are particularly advantageous since these produce monoolefins which can be utilized to make detergents having superior biodegradability and detergency. For example, a mixture containing a four or five homologue spread such as a C₁₀ to C₁₃ mixture, a C₁₁ to C₁₄, or a C₁₁ to C₁₅ mixture, provides excellent charge stocks. Moreover, it is preferred that the amount of non-normal hydrocarbons present in this hydrocarbon stream be kept at low levels. Thus, it is preferred that this stream contain greater than 90 wt. percent of normal paraffin hydrocarbon, with best results achieved at purities in the range of 96 to 98 wt. percent or more. In accordance with the present invention all of the charge stocks which are used in the present process contain a catalyst-deactivating cyclic contaminant which as discussed hereinbefore is typically a mixture of cyclic compounds with alkylaromatics, alkylindanes, and bi-cyclic aromatics being especially detrimental. Depending upon the source of the hydrocarbon stream these contaminants may be present in concentrations up to about 5 wt. percent. However, the typical concentration is substantially less than 1 wt. percent—about 0.1 wt. percent to about 0.8 wt. percent being representative of the situation encountered when the source of the charge stock is a preferred separation procedure employing molecular sieves. In addition, it is within the scope of the present invention to pretreat the hydrocarbon stream charged

thereto with a suitable method for removing cyclic compounds therefrom such as by contacting the hydrocarbon stream with a solution of fuming sulfuric acid at conditions effecting the removal of a major portion of the aromatics from the stream. Typically, this pretreatment procedure is effective to reduce the cyclic compounds down to a level of less than 1 wt. percent; however, they cannot be economically designed to remove all of the cyclic compounds.

In a preferred embodiment, the hydrocarbon stream is obtained by subjecting a hydrocarbon distillate, containing normal paraffin hydrocarbons, naphthenes, aromatics, and isoparaffins, to a separation operation employing one or more beds of molecular sieves having a pore size of about 5 Angstrom units, which sieves have the well-known capability to remove normal paraffin hydrocarbons from such a hydrocarbon distillate thereby producing a raffinate stream having a high concentration of the non-normal components originally present in the distillate stream. The normal paraffin hydrocarbons are thereafter recovered from the sieves, typically by displacement with a lower molecular weight normal paraffin hydrocarbon, to produce an extract stream containing normal paraffins and a minor amount of the displacing fluid. The extract stream is then typically subjected to a suitable fractionation operation designed to separate the displacing fluid therefrom and, in some cases, to adjust the boiling point range of the normal paraffin-containing stream. A preferred separation system for continuously producing this normal paraffin-containing hydrocarbon stream is described in the teachings of U.S. Patent No. 3,310,486 and reference may be had thereto for additional details.

Regardless of the exact mechanism of the separation operation used to produce a hydrocarbon stream suitable for charging to the process of the present invention, it is evident that a trade-off will exist between the quality of the extract stream, measured in weight percent normal paraffin hydrocarbon content, and the yield of the stream. Inevitably, in commercial practice this trade-off problem is solved by allowing a minor amount of non-normal components to appear in the extract stream feeding to the process of concern here. For example, a preferred procedure for producing this hydrocarbon stream involves charging a kerosene fraction boiling within the range of about 300° F. to about 500° F. to the separation system as described in U.S. Patent No. 3,310,486 and recovering therefrom a hydrocarbon stream containing a mixture of normal paraffins in the C₁₀ to C₁₅ range. Typically, this last procedure can be performed so that the hydrocarbon stream recovered therefrom contains 95 to 99 wt. percent normal paraffin hydrocarbons with the remainder being isoparaffins and cyclic contaminants. Subsequently acid treating of this extract stream can remove another portion of the non-normal hydrocarbons thereby producing a stream which is about 98 to 99.5 wt. percent pure normal paraffin hydrocarbons. However, the resultant stream inevitably contains a small amount of cyclic contaminants.

As pointed out hereinbefore, the catalyst used in the two dehydrogenation steps of the present invention comprises: an alumina component, a platinum group component, and an alkali component. Although it is not essential, it is generally preferred that the catalyst also contain a component selected from the group consisting of arsenic, bismuth, antimony, sulfur, selenium, tellurium, and compounds thereof.

The alumina component generally has an apparent bulk density less than about 0.50 gram per cc. with a lower limit of about 0.15 gram per cc. The surface area characteristics are such that the average pore diameter is about 20 to about 300 angstroms; the pore volume is about 0.10 to about 1.0 milliliter per gram; and the surface area is about 100 to about 700 square meters per gram. It may be manufactured by any suitable method including a well-known alumina sphere manufacturing procedure detailed in U.S. Patent No. 2,620,314.

The platinum group component is generally selected from the group of palladium, iridium, ruthenium, rhodium, osmium, and platinum, with platinum giving best results. The platinum group component may be used in a form of the elemental metal or as suitable compound such as the oxide, sulfide, etc., although it is generally preferred that it be used in a reduced state. The platinum group component is used in a concentration calculated on an elemental basis of about 0.05 wt. percent to about 5.0 wt. percent of the catalyst, with best results obtained at a level of about 0.5 to about 1.5 wt. percent. This component may be composited in any suitable manner with impregnation by water soluble compounds such as chloroplatinic acid being especially preferred.

The alkali component is selected from both alkali metals—cesium, rubidium, potassium, sodium, and lithium—and the alkaline earth metals—calcium, magnesium, and strontium. The preferred component is lithium. Generally, the alkali component is present in an amount based on the elemental metal of less than about 5% by weight of the total composite with a value in the range of about 0.01 wt. percent to about 1.5 wt. percent generally being preferred. In addition, the alkali component may be added to the alumina in any suitable manner, especially in an aqueous impregnation thereof, and thus suitable compounds are the chloride, hydroxides, nitrates, acetates, carbonates, etc.; for example, an aqueous solution of lithium nitrate gives excellent results. It may be added either before or after the other components are added or during alumina formation—for example, to an alumina hydrosol before the alumina carrier material is formed therefrom.

Preferably, the dehydrogenation catalyst contains a fourth component selected from the group consisting of arsenic, antimony, bismuth, sulfur, selenium, tellurium, and compounds thereof. Arsenic is particularly preferred. This component is typically used with good results in an amount of about 0.01% to about 1.0% by weight of the final composite. Moreover, this component is preferably present in an atomic ratio to the platinum group component of about 0.1 to about 0.8 with intermediate concentrations of about 0.2 to about 0.5 being highly effective. This component can be composited in any suitable manner—a particularly preferred way being via a water soluble impregnation solution such as a solution of arsenic pentoxide, etc.

This preferred catalytic composite is thereafter typically subjected to conventional drying and calcination treatments at temperatures in the range of 800° F. to about 1000° F. In addition, conventional prereduction and presulfiding treatment may be performed if desired. Additional details as to typical dehydrogenation catalysts suitable for use in the present invention are given in the teaching of U.S. Patent Nos. 3,291,755 and 3,310,599.

According to the present invention the hydrocarbon stream containing normal hydrocarbons and hydrogen are admixed, heated to conversion temperature, and charged to a first dehydrogenation zone containing the above described catalyst. Although the catalyst may be utilized in a fluidized state, or as a moving bed flowing counter-current to the hydrocarbon stream or as a slurry in the hydrocarbon stream, it is generally preferred to use a fixed bed of the catalyst comprising spherical particles of about $\frac{1}{16}$ inch diameter. The hydrogen used in the first dehydrogenation step may be once-through hydrogen or recycle hydrogen and it is generally used in an amount such that the ratio of moles of hydrogen to moles of hydrocarbon in the input stream is about 1 to about 20 with about 5 to about 15 giving good results. In some cases, a relatively inert diluent such as water, methane, etc. may also be charged to this first dehydrogenation step. The function of this first step is to remove a portion of the contaminants from the hydrocarbon stream charged thereto and to effect selective catalytic dehydrogenation of a portion of the normal paraffins. Accordingly, this first dehydro-

genation step is conducted at a temperature of about 750° F. to about 1100° F., with a preferred range being about 800° F. to about 950° F. at a pressure of about 10 p.s.i.g. to about 100 p.s.i.g., and at a liquid hourly space velocity of about 10 to 40 hr.⁻¹. The exact selection of conditions within these ranges is continuously adjusted in order to insure continuous removal of a portion of the cyclic contaminants from the hydrocarbon stream, and the catalyst is periodically regenerated or replaced when the build-up of carbonaceous deposits, produced at least in part from their undesired contaminants, compromises its intended function. A preferred procedure for accomplishing this regeneration or replacement is a swing reactor system wherein at least one reactor is always on stream while one or more reactors are being regenerated by conventional oxygen-treating techniques.

An effluent stream is then withdrawn from the first dehydrogenation step, cooled, and separated in a conventional separating zone into a hydrogen-rich vapor phase and a hydrocarbon-rich liquid phase containing unreacted normal paraffin hydrocarbons and the normal mono-olefin hydrocarbons. At least a portion of the hydrogen-rich gaseous phase withdrawn from the separating zone is typically recompressed and recycled to the dehydrogenation steps of the present invention. The hydrocarbon-rich liquid phase withdrawn from this separating zone constitutes a first mixture of the normal mono-olefins and unreacted normal paraffin hydrocarbons. This first mixture is then typically combined with a second mixture produced from the effluent from the second dehydrogenation step of the present invention, the source of which will be evident from the discussion below. Although separate separation zones may be used to remove hydrogen from the effluent streams from the two dehydrogenation steps, it is generally most convenient to perform the hydrogen separation in a single zone when the pressure utilized in the two dehydrogenation steps is substantially the same. However, when the two dehydrogenation steps are operated at different pressure it is preferred to use the hydrogen separating zones for the purpose of pressure control and accordingly, two hydrogen separation zones are used. Regardless of whether one or two hydrogen separating steps are utilized, the effluent from the first dehydrogenation step will provide a first mixture of the normal mono-olefins and the unreacted normal paraffins and the effluent from the second dehydrogenation step will provide a second mixture of similar composition. These two mixtures are then commingled either during the hydrogen separation step or immediately thereafter.

After the hydrogen is separated, the resulting mixture of normal mono-olefins and unreacted normal paraffins is passed to a separation step designed to remove the normal mono-olefins therefrom. In general, any suitable method may be used to separate the normal mono-olefins from these mixtures including physical techniques such as selective adsorption, selective absorption, extractive distillation, etc., or chemical techniques which depend on the relatively high reactivity of the mono-olefins as contrasted with the relatively inert character of the normal paraffins. For example, one physical method of separation involves passing the mixture through a bed of suitable adsorbent which selectively retains the normal mono-olefins. Typical adsorbents of this type include activated silica gel in particle form, activated charcoal, activated alumina, molecular sieves of 10 A. pore size, etc. The resultant mono-olefin-free stream is then passed to the second dehydrogenation step of the present invention.

A preferred chemical method for removing the normal mono-olefins from these mixtures involves an alkylation step where the olefin-paraffin mixture is commingled with an alkylatable aromatic, benzene being preferred, and charged to an alkylation zone containing a suitable acid-acting alkylation catalyst such as an anhydrous solution of hydrogen fluoride. The mono-olefins react in the alkyla-

tion zone with the alkylatable aromatic while the normal paraffins remain substantially unchanged. The unreacted normal paraffins can then be easily recovered from the effluent from the alkylation zone by a suitable fractionation system and passed to the second dehydrogenation step. For additional details as to suitable catalysts, conditions, and mechanics of preferred alkylation steps, reference may be had to U.S. Patent Nos. 3,249,650 and 3,200,163.

Following the removal of the normal mono-olefins from the mixture, a stream containing at least a portion of the unreacted normal paraffins contained in these mixtures is passed to the second dehydrogenation step of the present invention. This step preferably comprises passing the unreacted normal paraffins and hydrogen into contact with a selective hydrogenation catalyst of the type hereinabove characterized. As in the first step this catalyst is preferably utilized as a fixed bed of particles having a maximum dimension of about $\frac{1}{16}$ inch. The function of this second dehydrogenation step is to selectively dehydrogenate the unreacted normal paraffins and to suppress undesired side reactions leading to a non-normal product which, for the reasons previously explained, can greatly accelerate the deactivation of this catalyst. Accordingly, the conditions utilized in this second step are ordinarily chosen to produce a conversion of about 5 to about 15 wt. percent of the unreacted normal paraffins being charged thereto on a per pass basis. The exact conditions utilized in this step are selected from the range given above in conjunction with the discussion of the first dehydrogenation step with the principal difference being the rate of change of the parameters with respect to time necessary to run at constant conversion levels: this second step being much more stable due to the absence of the cyclic contaminant.

An effluent stream containing normal mono-olefins corresponding to the carbon structure of the unreacted normal paraffins, hydrogen, and unreacted normal paraffins is then withdrawn from this second dehydrogenation step, cooled, and passed to a hydrogen separating zone. Here a hydrogen-rich gas phase is withdrawn as before and a second mixture of the normal mono-olefins and normal paraffins is formed. As indicated hereinbefore, this second mixture is then passed to the mono-olefin removing step.

The attached drawing illustrates a flow diagram for one preferred embodiment of the present invention and is introduced to demonstrate further the novelty, mode of operation, and utility of the present invention.

Referring now to the drawing, a hydrocarbon stream enters the process through line 1. This stream contains 0.3 wt. percent n-C₁₀, 26.6 wt. percent n-C₁₁, 31.3 wt. percent n-C₁₂, 25.0 wt. percent n-C₁₃, 13.2 wt. percent n-C₁₄, and 0.4 wt. percent n-C₁₅. In addition, this hydrocarbon stream contains a minor amount of non-normal hydrocarbons comprising mono-olefins, monocyclic paraffins, diolefins, dicyclic paraffins, and alkyl aromatics of which about 1 wt. percent are catalyst deactivating cyclic contaminants. Just prior to the entrance of the hydrocarbon stream into the first dehydrogenation zone 2 it is admixed with about 9.0 moles of hydrogen per mole of hydrocarbon contained therein, heated to the desired conversion temperature by suitable heating means (not shown) and passed into zone 2 in either upward, downward or radial flow.

Dehydrogenation zone 2 contains a fixed bed of $\frac{1}{16}$ inch spherical catalyst particles prepared according to the method given in U.S. Patent No. 3,291,755 and containing on an elemental basis, 0.76 wt. percent platinum, 0.041 wt. percent arsenic, 0.55 wt. percent lithium, all composited with gamma-alumina carrier material. Furthermore, the catalyst has an ABD of 0.46, a surface area of about 145 m.²/gm. and a pore volume of 0.40 ml./gm. Zone 2 is operated at an outlet pressure of about 30 p.s.i.g., a liquid hourly space velocity of about 32 and a

conversion temperature which is continuously selected from the range of about 850° F. to about 950° F. in order to remove a portion of the contaminants contained in the input hydrocarbon stream and which results in a conversion level to normal mono-olefins of about 5 to 15 wt. percent based on fresh feed. An effluent stream is then withdrawn from zone 2 via line 3 and passed to separating zone 4.

In separating zone 4 a hydrogen-rich gaseous phase separates from a hydrocarbon liquid phase. In addition, a second effluent stream (the source of which will be described below) of similar composition to the one entering through line 3 is passed into zone 4 via line 16. The hydrogen-rich gaseous phase is withdrawn from separating zone 4 via line 5, passed through compressive means (not shown) and recycled to dehydrogenation zone 2 and dehydrogenation zone 15. Moreover, excess recycle gas is vented from the system via line 18.

The liquid hydrocarbon phase in zone 4 is withdrawn via line 6 and at least a portion of it is charged to the alkylation zone 7. In addition, an aromatic stream is charged to alkylation zone 7 via line 14 through line 6. In this case the alkylatable aromatic is substantially pure benzene. The catalyst used in alkylation zone 7 is substantially anhydrous hydrogen fluoride, which in the course of use is degraded to a steady-state acidity of about 93%. Conditions used in zone 7 are: a mole ratio of benzene to total olefin in the influent hydrocarbon stream of about 10, a volume ratio of hydrogen fluoride to the total influent hydrocarbon stream of about 1, a pressure sufficient to maintain the reactants and catalyst in liquid phase, a temperature of about 80° F. to about 140° F., and a residence time of about 10 minutes. Suitable provision is made within alkylation zone 7 to remove excess heat generated by the reaction therein. After separation of a hydrogen fluoride acid phase, an effluent stream containing phenyl-substituted normal paraffins, unreacted normal paraffins, unreacted benzene, and a minor amount of side reaction products produced in the alkylation zone such as diphenylalkanes, alkylindanes, alkyltetralins, alkylfluorenes, etc. is withdrawn from alkylation zone 7 and passed via line 8 to separating system 9.

The function of separating system 9 is to separate the stream being charged thereto into its constituent parts. This separation operation is conveniently performed in a suitable fractionation train, typically comprising three conventional fractionation columns: the first, taking benzene overhead via line 13 wherein it is recycled to alkylation zone 7; the second operating on the bottoms from the first, after suitable treatment for alkylfluoride removal, and taking an unreacted normal paraffin stream over-head which via line 10 is passed to the second dehydrogenation zone 15; and the third taking phenyl-substituted alkanes over-head, via line 11, with a minor amount of heavy alkylate recovered as bottoms, via line 12.

The unreacted normal paraffin hydrocarbon stream flowing through line 10 is commingled with a hydrogen stream at the junction of line 10 with line 17 in an amount of about 9 moles of hydrogen per mol of hydrocarbon. The resulting mixture is heated to the desired conversion temperature (by means not shown) and passed to second dehydrogenation zone 15. Zone 15 contains a fixed bed of catalyst which is identical to that utilized in zone 2 with the exception that substantially more catalyst is used in zone 15 than in zone 2. Zone 15 is operated at an outlet pressure of 30 p.s.i.g., a liquid hourly space velocity of about 32 and a conversion temperature which is selected from the range of about 850° F. to about 1000° F. in order to maintain a conversion level of about 10 wt. percent.

An effluent stream is then withdrawn from zone 15 via line 16 and passed to separating zone 4 wherein it is separated into a hydrocarbon-rich gaseous phase and

a mixture of mono-olefins and unreacted normal paraffins as was previously indicated.

The effluent from the first dehydrogenation zone is continuously monitored to determine concentration of the cyclic contaminant contained therein. After about thirty barrels of fresh charge per pound of catalyst contained in zone 2 the concentration of the cyclic contaminants contained in the stream flowing through line 3 starts to increase, and at this point zone 2 is replaced by a twin reactor containing a fresh load of the dehydrogenation catalyst. The mechanics and piping for a swing bed operation are well known and will not be repeated here. The reactor containing the deactivated catalyst is then subjected to a conventional oxygen regenerating treatment designed to remove carbonaceous deposits therefrom. Operation in this manner is continued with periodic switching between the two reactors employed in zone 2, and it is found that the dehydrogenation reaction conducted in zone 15 is deactivating at a rate of 0.25° F. per barrel of hydrocarbon charged thereto per pound of catalyst contained therein. In addition the conversion attained therein is stable at approximately 10.0 wt. percent. Furthermore the quality and yield of the phenyl-substituted normal paraffins recovered via line 11 indicates that non-normal paraffins are not being synthesized in any significant amount in the process: that is, selectivity is being maintained at a high level.

I claim as my invention:

1. A catalytic process for dehydrogenating a hydrocarbon stream containing normal paraffin hydrocarbons, having about 6 to about 20 carbon atoms, and a catalyst-deactivating cyclic contaminant, said process comprising the steps of:

- (a) contacting, in a first dehydrogenation zone, the hydrocarbon stream and hydrogen with a first catalyst containing a platinum group component, an alkali component, and an alumina component, at dehydrogenation conditions selected to form a first effluent stream containing normal mono-olefins having the same number of carbon atoms as said normal paraffin hydrocarbons, hydrogen, and unreacted normal paraffin hydrocarbons;
- (b) withdrawing said first effluent stream from said zone and separating hydrogen therefrom to obtain a first mixture of the normal mono-olefins and unreacted normal paraffin hydrocarbons;
- (c) removing said normal mono-olefins from said first mixture to form a stream containing unreacted normal paraffin hydrocarbons;
- (d) contacting, in a second dehydrogenation zone, said last stream and hydrogen with a second catalyst having a platinum group component, an alkali component, and an alumina component at dehydrogenation conditions selected to produce a second effluent

stream containing normal mono-olefins, hydrogen and unreacted normal paraffin hydrocarbons; and, (e) withdrawing said second effluent stream from said second zone, separating hydrogen therefrom to form a second mixture of the normal mono-olefins and unreacted normal paraffin hydrocarbons, and passing said second mixture to said removing step.

2. The process of claim 1 wherein said first and second catalysts contain a component selected from the group consisting of arsenic, antimony, bismuth, sulfur, selenium, tellurium, and compounds thereof.

3. The process of claim 2 wherein said first and second catalyst are a composite of alumina, about 0.01 wt. percent to about 1.5 wt. percent of lithium, about 0.05 wt. percent to about 5.0 wt. percent of platinum, and arsenic in an amount of about 0.1 to about 0.8 atom of arsenic per atom of the platinum.

4. The process of claim 1 wherein said contaminant is an alkylaromatic hydrocarbon.

5. The process of claim 1 wherein said contaminant is an alkylindane.

6. The process of claim 1 wherein said contaminant is a polycyclic aromatic hydrocarbon.

7. The process of claim 1 wherein said removing step comprises: contacting said first mixture and an alkylatable aromatic with an alkylation catalyst at alkylation conditions effective to produce an effluent stream containing alkylaromatics and unreacted normal paraffin hydrocarbons, and separating therefrom the stream containing the unreacted normal paraffin hydrocarbons.

8. The process of claim 7 wherein said alkylation catalyst is anhydrous hydrogen fluoride.

9. The process of claim 1 wherein said removing step comprises contacting said first mixture with an adsorbent material which selectively adsorbs the normal mono-olefins and withdrawing, from contact with the adsorbent material, the stream containing the unreacted normal paraffin hydrocarbons.

10. The process of claim 1 wherein said hydrocarbon stream contains a mixture of C₁₀ to C₁₅ normal paraffin hydrocarbons.

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