

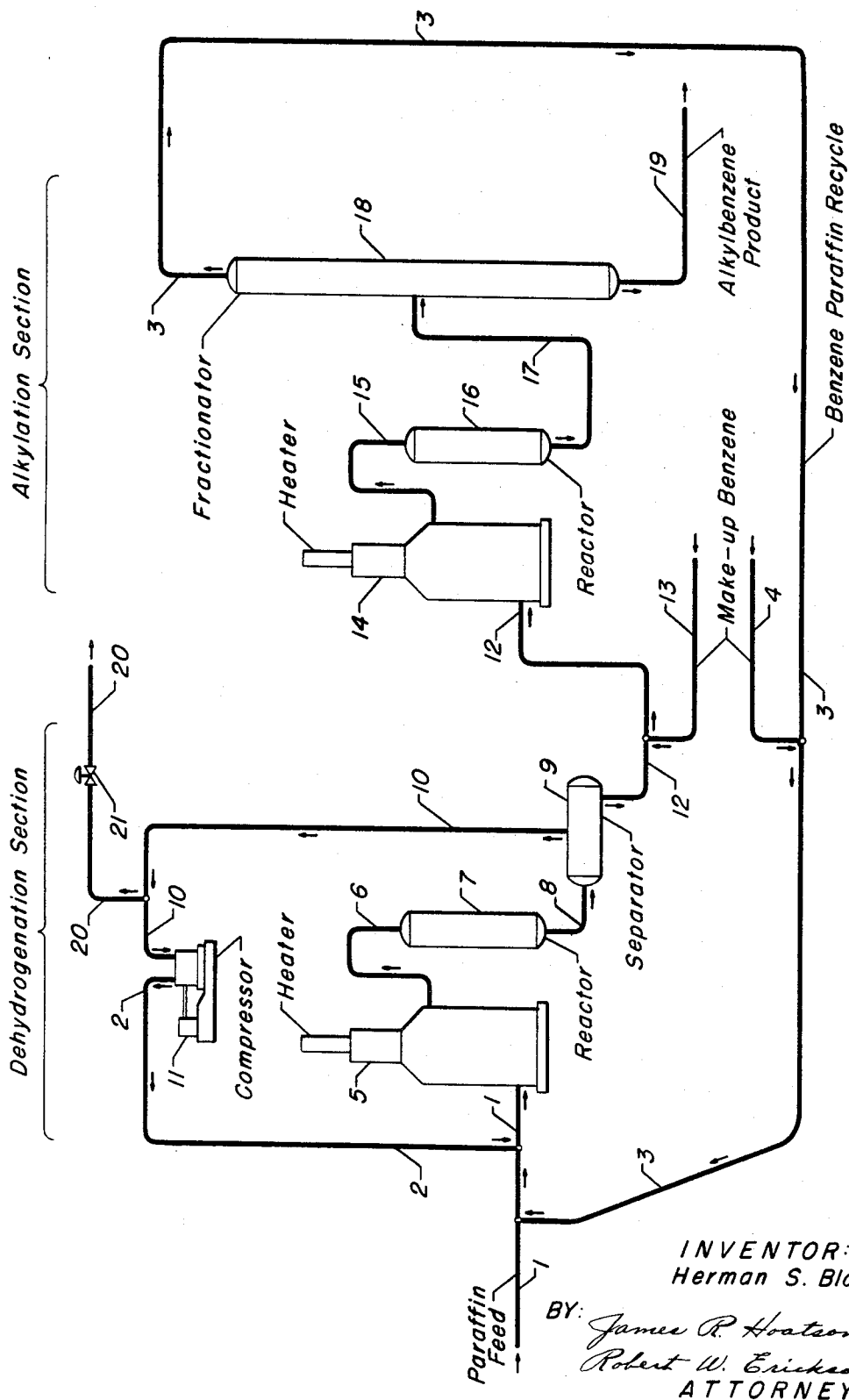
Nov. 26, 1968

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3,413,373

PROCESS FOR PRODUCING ALKYLAROMATIC HYDROCARBONS

Filed Sept. 12, 1966



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3,413,373

PROCESS FOR PRODUCING ALKYLAROMATIC HYDROCARBONS

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Filed Sept. 12, 1966, Ser. No. 578,766
10 Claims. (Cl. 260—671)

ABSTRACT OF THE DISCLOSURE

Production of alkylaromatic hydrocarbons via a combination process involving (1) dehydrogenation of a paraffin, (2) alkylation of a mono-nuclear aromatic with the resulting olefin and (3) separation and recycle of unreacted paraffinic and aromatic hydrocarbons to the dehydrogenation step.

The present invention relates to a process for the production of alkylaromatic hydrocarbons, and especially those in which the aryl nucleus is mono-cyclic. More specifically, the inventive concept described herein involves a novel combination process encompassing the dehydrogenation of paraffins to mono-olefins containing the same number of carbon atoms, and the use of said mono-olefin in the alkylation of mono-nuclear aromatic hydrocarbons. bon atoms per molecule are dehydrogenated to a normal paraffins containing from about three to about twenty carbon atoms per molecule are dehydrogenated to a normal mono-olefin (having the same number of carbon atoms), which mono-olefin is employed for alkylating an alkylatable aromatic hydrocarbon, and especially mono-nuclear aromatic hydrocarbons. The present invention offers unusual advantages in the preparation of alkylbenzenes in which the alkyl group contains from about ten to about fifteen carbon atoms per molecule, and which are intended for use in the subsequent production of detergents, and especially biodegradable soft detergents.

Alkylaromatic hydrocarbons enjoy widespread use in a variety of commercial industries including the petroleum, petrochemical, heavy chemical, detergent, etc. Exemplary of such uses are the following: cumene, formed by alkylating benzene with propylene, is oxidized to cumene hydroperoxide which is readily decomposed to phenol and acetone; alkylated aromatics, boiling within the gasoline boiling range possess high anti-knock characteristics, and are extensively used as aviation fuel; alkylaryl sulfonates, such as sodium tridecylbenzene sulfonate, are used as anionic synthetic detergents; tert-butylbenzene is employed principally in organic synthesis; and, di-long chain benzenes are used to make heavy metal sulfonate salts for lube oil detergents. These, as well as many other uses for alkylaromatic hydrocarbons, are well known and well defined in the literature, no attempt is made herein to be exhaustive.

The principal object of the present invention is to provide a combination process in which the dehydrogenation of paraffinic hydrocarbons may be effected at close to equilibrium conversion with unusual operational stability, and wherein the alkylation of an aromatic hydrocarbon with the resulting olefinic hydrocarbon is conducted in an economically beneficial manner.

Another object is to produce alkylaromatic hydrocarbons from paraffins and aromatics, and especially to produce alkylbenzene hydrocarbons having an alkyl group containing from ten to about twenty carbon atoms. A specific object is to produce C₁₀ to C₁₅ alkylbenzenes for ultimate use in the preparation of biodegradable soft detergents of the alkylbenzene sulfonate class. Other objec-

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tives of my invention will become apparent from the following discussion and examples.

In a broad embodiment, the present invention relates to a combination process for the production of an alkylaromatic hydrocarbon, which process comprises the steps of: (a) dehydrogenating a paraffinic hydrocarbon in a catalytic dehydrogenation reaction zone maintained under dehydrogenation conditions and in the presence of hydrogen and an aromatic hydrocarbon; (b) separating a hydrogen-rich gaseous phase from the resulting dehydrogenation product effluent and passing the remainder of said effluent, including unreacted paraffinic hydrocarbon and said aromatic hydrocarbon into an alkylation reaction zone maintained under alkylation conditions and in contact therein with an acid-acting alkylation catalyst; and, (c) separating the resulting alkylation product effluent to provide a mixture of said paraffinic hydrocarbon and unreacted aromatic hydrocarbon, recycling said mixture to said dehydrogenation zone, and recovering an alkylaromatic hydrocarbon product.

A more specific embodiment of the present invention is directed toward a process for the production of a mono-nuclear alkylaromatic hydrocarbon, which process comprises the steps of: (a) dehydrogenating a normal paraffinic hydrocarbon containing from about ten to about twenty carbon atoms per molecule in contact with a noble metal-containing catalytic composite disposed in a dehydrogenation reaction zone, under dehydrogenation conditions, and in the presence of hydrogen and a mono-nuclear aromatic hydrocarbon, the latter present in a mol ratio to said normal paraffin of from about 0.5:1 to about 2:1; (b) separating a hydrogen-rich gaseous phase from the resulting dehydrogenation product effluent and passing the remainder of said effluent, including unreacted normal paraffinic hydrocarbon and said mono-nuclear aromatic hydrocarbon into a hydrogen fluoride catalyzed reaction zone, maintained under alkylation conditions; (c) treating the resulting alkylation product effluent to recover a substantially hydrogen fluoride-free hydrocarbon mixture; and, (d) separating said mixture to provide a hydrocarbon stream rich in unreacted aromatic hydrocarbon and said normal paraffin, recycling said stream to said dehydrogenation reaction zone, and recovering a mono-nuclear alkylaromatic hydrocarbon.

With respect to the dehydrogenation section of the present combinative process, the charge stock may be any normal paraffinic hydrocarbon, or iso-paraffinic hydrocarbon with limited branching, having from about three to about twenty carbon atoms per molecule. Thus, the charge stock may be selected from the propane, butane, isobutane, pentane, isopentane, hexane, heptane, iso- and normal octane, undecane, dodecane, tridecane, pentadecane, hexadecane, heptadecane, octadecane, mixtures thereof, etc. Since the longer chain normal paraffins, having from about seven to about twenty carbon atoms per molecule, and particularly those having from about ten to about fifteen carbon atoms, can be successfully dehydrogenated to form the intermediate monoolefins for use in the alkylation section to produce the alkylaromatic intermediate of a sulfonated detergent, such longer chain, normal paraffins are particularly preferred.

Although the strictly thermal conversion of paraffins to the corresponding olefins can be effected at a sufficiently high temperature, commercial acceptability dictates the utilization of a suitable dehydrogenation catalyst from the standpoint of product quality and the yield thereof. While it is recognized that prior art dehydrogenation processes are replete with a multitude of suggestions for suitable catalytic composites, additional benefits are afforded the use of the present invention in conjunction with a particular catalytic composite. The prior art catalysts generally consist of one or more metallic components select-

ed from the group of metals from Groups VI and VIII of the Periodic Table, and compounds thereof. Such prior art catalysts are usually composited with a carrier material comprising one or more refractory inorganic oxides selected from the group of alumina, silica, zirconia, magnesia, thoria, hafnia, boria, titania, etc. Although the present invention will offer advantages to a dehydrogenation process regardless of the character of the catalyst employed therein, the overall results of the present combinative process are enhanced through the utilization of a noble metal-containing catalyst. When the dehydrogenation of normal paraffinic hydrocarbons is being conducted at close to equilibrium conversion, regardless of the character of the catalyst being employed, various side reactions including cracking and skeletal isomerization are also effected. A significant degree of conversion to di-olefins and tri-olefins results, and unnecessary quantities of the lower molecular weight gases, including methane and ethane, will be produced. These, as well as other undesired side reactions, detrimentally affect the efficiency of conversion of the paraffin to the desired olefin, and, therefore, tend to adversely alter the economic considerations involved in the process. When the dehydrogenation portion of the present combination process is effected, I have observed that there is essentially no skeletal isomerization of the resulting normal mono-olefins to branched-chain olefins. Generally, the cracked products, as well as dienes and trienes are produced only in trace quantities.

The particularly preferred catalytic composite for the dehydrogenation section of the present invention comprises alkalinized alumina containing a Group VIII noble metal and a component from the group of arsenic, antimony, bismuth and compounds thereof. Furthermore, the catalytic composite should be non-acidic, and especially halogen-free. Thus, a non-acidic carrier is combined with a Group VIII noble metal component, an alkali metal component, and, for example, arsenic. Although alkaline-earth metallic components, including calcium, magnesium, and/or strontium, may be employed, the alkali metals, cesium, rubidium, potassium, sodium and especially lithium are preferred. The Group VIII noble metal, palladium, iridium, ruthenium, rhodium, osmium, and especially platinum, will be utilized in an amount of from about 0.05% to about 5.0%, calculated as if existing within the final composite as the elemental metal. The alkali metals will be employed in an amount generally not exceeding 5.0% by weight; in order to achieve a proper balance between inhibiting the occurrence of side reactions and imparting the desired degree of stability, the alkali metals will generally be employed in significantly lower concentrations. Therefore, they will generally be present in a concentration within the range of from about 0.01% to about 1.5% by weight, also calculated as if existing within the composite as the element.

The fourth component of the catalytic composite, in addition to the alkali metal, alumina, and the Group VIII metallic component, is selected from the metals of Group V-A of the Periodic Table, and compounds thereof. The use of the term "Group V-A," in the present specification and in the appended claims, alludes to the Periodic Chart of the Elements, Fisher Scientific Company, 1953. It is recognized that these elements are often referred to as "non-metallic" as the result of their peculiar characteristics. For the sake of convenience and consistency, such elements are herein referred to as "metals". The metallic component selected from the group of arsenic, antimony, bismuth and compounds thereof will be present in an atomic ratio to the Group VIII metallic component in the range of from about 0.1 to about 0.8. Experience has indicated that intermediate concentrations may be, and are preferably employed; the atomic ratio of the Group V-A metal to the Group VIII metal will generally be in the range of from about 0.2 to about 0.5.

Although it has been shown that supported platinum-

containing catalysts are very active in promoting dehydrogenation of paraffinic hydrocarbons, they inherently possess additional properties which are objectionable, and stem from the overall activity and ability for platinum to promote other kinds of reactions. The alkali metal component is utilized for the primary purpose of effectively inhibiting a substantial amount of cracking and skeletal isomerization reactions, and to neutralize at least a portion of the inherent acid functions possessed by platinum as well as that of the carrier material; however, sufficient cracking activity remains such that higher temperature operations to increase conversion is precluded. Furthermore, there still is present the capability of the platinum to promote cyclization reactions. The primary function of the catalytic attenuator, arsenic, antimony, and/or bismuth, is actually two-fold. That is, the catalyst attenuator is specifically intended to poison the platinum to the extent that its residual cracking activity is virtually completely curtailed, and the tendency to promote other side reactions, particularly cyclization, is substantially eliminated. The uniqueness of these attenuators resides in the fact that the dehydrogenation activity of the platinum component is barely affected.

Another advantage afforded through the utilization of this particular catalytic composite resides in the suppression of the tendency for the desired constituents of the product stream to undergo further dehydrogenation to dienes and trienes. The presence of minor quantities of dienes within the mono-olefinic product is not particularly troublesome with respect to the ultimate use of the olefin. For example, when the olefin product is alkylated with benzene, the diene tends either to undergo cyclization to alkylindanes or alkyltetralins, or to form diphenyl alkanes, of which the first two may be utilized as part of the alkylate product and the latter easily separated from the desired product. Although spectroscopic methods of analysis have not detected any branched-chain olefins in the product resulting from the dehydrogenation section of the present invention, up to about 5.0% or even 10.0% of mono-branching (based upon the mono-olefin) would not be objectionable for ultimate use in preparing biodegradable alkylbenzene sulfonate detergents. In the case, however, of alkylsulfate detergents, branching in even small quantities leads to unstable tertiary sulfates. In view of the high degree of stability of some of the alkylsulfate detergents which I have prepared from the mono-olefinic product from the dehydrogenation section, the degree of branching within said product must necessarily be exceedingly small.

The dehydrogenation portion of the present combination process may be further characterized through the operating conditions under which it is conducted. These conditions include a pressure of from about 10 to about 50 p.s.i.g., and preferably from about 15 to about 40 p.s.i.g. The temperature at the inlet to the reaction zone is preferably controlled at a level within the range of from about 800° F. to about 930° F., and the paraffin charge rate is such that the liquid hourly space velocity is within the range of from about 12 to about 40. In addition, the paraffinic charge stock is diluted by an aromatic hydrocarbon, and preferably that aromatic hydrocarbon which is intended to be alkylated in the alkylation section of the present process, the source of which is hereinafter described. The aromatic hydrocarbon is employed in an amount to result in a mol ratio, with respect to the paraffinic hydrocarbon, within the range of from about 0.5 to about 2.0, and is based only on the fresh paraffinic charge. In a co-pending application, filed of even date herewith, Ser. No. 578,504, I have shown that the addition of an aromatic hydrocarbon to the dehydrogenation reaction zone not only increases the degree of conversion of the paraffinic hydrocarbon, but improves the selectivity of such conversion to the desired normal mono-olefinic product. Furthermore, there is experienced a more stable operation with respect to the conversion and selec-

tivity thereof. Greater quantities of the aromatic hydrocarbon than that herein set forth do not appear to enhance further the results obtained, while lesser quantities result in a product effluent in which aromatic hydrocarbon to mono-olefinic hydrocarbon mol ratio is less than that desired for the alkylation of the aromatic hydrocarbon in the alkylation section. The dehydrogenation improvement is believed to be due to the characteristics of the aromatic hydrocarbon which enables it to be more readily and strongly sorbed relative to either paraffin or mono-olefin. Thus, the aromatic hydrocarbon quickly displaces product molecules from the catalyst surface, thereby reducing the degree to which secondary reactions may be effected.

The second section of the present process comprises an alkylation reaction zone and a product recovery system which functions to separate the alkylaromatic hydrocarbon from the paraffins and unreacted aromatic hydrocarbons. The alkylation section may be any acidic catalyst reaction system such as a hydrogen fluoride-catalyzed reaction system, or one which utilizes a boron halide in a fixed-bed reaction system. Many aromatic hydrocarbons are utilizable as alkylatable aromatic hydrocarbons within the combination process of the present invention. Preferred aromatic hydrocarbons are monocyclic aromatic hydrocarbons, that is, benzene hydrocarbons. Thus, suitable aromatic hydrocarbons include benzene, toluene, ortho-xylene, meta-xylene, para-xylene, ethylbenzene, ortho-ethyltoluene, meta-ethyltoluene, para-ethyltoluene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, normal propylbenzene, etc. Other suitable alkylatable aromatic hydrocarbons include those with two or more aryl groups such as diphenyl, diphenylmethane, triphenylmethane, stilbene, etc. Aromatic hydrocarbons containing condensed benzene rings, including naphthalene, alpha-methylnaphthalene, betamethylnaphthalene, etc., anthracene, phenanthrene, etc., may be employed. Of the foregoing alkylatable aromatic hydrocarbons for use as a starting material in the process of the present invention, the benzene hydrocarbons are preferred, and of these benzene itself is particularly preferred.

The combination process of the present invention may be clearly understood upon reference to the accompanying drawing. The drawing is presented to illustrate an embodiment of the present invention involving the use of benzene, for the purpose of making alkylbenzene product, and it is not intended to be unduly limiting upon the present invention. Within the drawing, various flow valves, control valves, coolers, condensers, overhead reflux condensers, pumps, compressors, etc., have been eliminated or reduced in number as not being essential to a complete understanding of the present process. The utilization of such miscellaneous appurtenances will be immediately recognized by those having expertise in the art of chemical processing.

Referring now to the figure, a paraffinic charge stock, for example a mixture of normal paraffins containing from about 10 to about 13 carbon atoms per molecule, is introduced to the process via line 1. Prior to entering heater 5, the normal paraffin charge stock is admixed with benzene from line 3, the source of which is hereinafter set forth, and a recycle hydrogen-rich gaseous phase from line 2, the resulting mixture passing through heater 5 and line 6 into reactor 7. Reactor 7 is maintained under dehydrogenating conditions including a temperature within the range of from about 750° F. to about 1100° F., intermediate temperatures of from about 800° F. to about 930° F. being preferred. Pressures greater than about 40 p.s.i.g. do not appear to effect additional benefits and are not, therefore, generally employed, the preferred pressure range being about 15 to about 40 p.s.i.g. It has been found that the liquid hourly space velocity defined as volumes of paraffin charge per hour per volume of catalyst disposed within the reaction zone) is above about 10. With

respect to the longer chain paraffinic hydrocarbons, that is, those containing from about ten to about twenty carbon atoms per molecule, liquid hourly space velocities of from about 12 to about 40 further enhance the results obtained, particularly with respect to the stability of the catalytic composite. Although prior art dehydrogenation processes generally employ a hydrogen concentration within the reaction zone of from about 1.0 to about 20 mols per mol of hydrocarbon charge stock, through the use of the present invention, the hydrogen concentration resulting from the recycled gaseous phase in line 2, can be lowered to a level below about 15, and, in fact, hydrogen recycle ratios in the range of from about 1.0 to about 10 are permitted without incurring detrimental effects such as rapid carbonization of the catalytic composite.

The total dehydrogenation product effluent, including unreacted paraffinic hydrocarbons, benzene from line 3, and the normal mono-olefinic product, is removed from reactor 7 through line 8, passing thereby into a suitable high pressure separator 9. A gaseous phase is withdrawn through line 10 via compressor 11 and is recycled to combine with the paraffinic feed via line 2. Since the dehydrogenation reaction produces hydrogen, the operating pressure on reactor 7 is maintained by withdrawing a portion of the gaseous phase from line 10 through line 20 containing pressure control valve 21. The normally liquid hydrocarbons are withdrawn from separator 9, generally on liquid level control, through line 12. By maintaining the benzene concentration in reactor 7 within the range of from about 0.5 to about 2.0 mols per mol of fresh paraffin charge stock entering via line 1, the mol ratio of benzene to the mono-olefin in line 12 will be at least about 5:1 particularly preferred for effecting the alkylation thereof. Make-up benzene is preferably added to the process via line 4 into line 3, to be admixed with the paraffin feed in line 1. However, for the purposes of controlling the ratio of benzene to the mono-olefinic hydrocarbon, in line 12, at least a portion of the make-up benzene may be added to the process through line 13.

In any event, the normally liquid hydrocarbon mixture passes through heater 13 and line 15 into alkylation reactor 16. Since the hydrogen fluoride alkylation process may be effected at temperatures of from 30° F. to about 125° F., and the stream in line 12 will be at a temperature intermediate this range, the vessel indicated in the drawing as heater 14, may, in fact, be a cooler or other type heat-exchanger. Likewise, the fixed-bed, boron trifluoride alkylation is often effected at temperatures lower than the material in line 12. Such modification to the illustrated embodiment will be recognized by those having expertise in this area. The total alkylation product is withdrawn from reactor 16 through line 17, and passes into fractionator 18. Fractionator 18 serves to separate the alkylbenzene product from the total alkylation reaction product effluent. The alkylbenzene product is withdrawn from fractionator 18 through line 19, while the unreacted benzene and the non-dehydrogenated paraffinic hydrocarbons are withdrawn as a mixture overhead through line 3 to be recycled to combine with the paraffin feed in line 1.

The present process involves the alkylation of an alkylatable aromatic hydrocarbon with an olefinic hydrocarbon. When the alkylation section makes use of hydrogen fluoride, it may be conducted substantially as set forth in U.S. Patent No. 3,249,650, although relating to an isoparaffin alkylation process. Briefly, the alkylation reaction, when conducted in the presence of hydrogen fluoride catalyst is such that the catalyst to hydrocarbon volume ratio within the alkylation reaction zone is from about 0.5 to about 2.5. Ordinarily, anhydrous hydrogen fluoride will be charged to the alkylation system as fresh catalyst; however, it is conceivably possible to utilize hydrogen fluoride containing as much as 10.0% water or more. In order to reduce the tendency of the olefins to

undergo polymerization, the mol ratio of the aromatic hydrocarbon to the olefinic hydrocarbon is maintained at a value greater than 1.0, and preferably from about 3:1 to 15:1. The alkylation reaction conditions, as catalyzed by hydrogen fluoride, include a temperature of from about 0° to about 200° F., and preferably from about 30° F. to about 125° F. The pressure maintained on the alkylation system is ordinarily just at a level sufficient to maintain the hydrocarbons and catalyst in substantially liquid phase, that is, from about atmospheric to about 40 atmospheres. The contact time within the alkylation reactor is conveniently expressed in terms of space-time, which is defined as the volume of catalyst within the reactor contacting zone divided by the volume rate per minute of hydrocarbon reactions charged to the zone. Usually the space-time will be less than 30 minutes and preferably less than about 15 minutes.

When the alkylation section of the combination process of the present invention is effected as a fixed-bed unit utilizing a boron halide catalyst, such as boron trifluoride, the operating conditions will be substantially those as set forth in U.S. Patent No. 3,200,164, notwithstanding that this patent teaches an alkylation-transalkylation process for the production of ethylbenzene. The amount of boron trifluoride is relatively small, and generally not more than about 1.0 gram of boron trifluoride per gram mol of the mono-olefin. The boron trifluoride alkylation reaction zone is of the conventional type and contains a boron trifluoride-modified inorganic oxide selected from diverse inorganic oxides including alumina, silica, boria, oxides of phosphorus, titania, zirconia, zinc oxide, magnesia, mixtures of two or more, etc. The operating conditions may be varied over a relatively wide range, the precise selection generally being dependent upon the character of both the olefinic hydrocarbon as well as the aromatic hydrocarbon. In any event, the alkylation reaction may be effected at a temperature of from about 0° to about 250° C., and under a pressure of from about 15 to about 200 atmospheres or more. The pressure is usually selected to maintain the alkylatable aromatic compound in substantially liquid phase at the operating temperature. The liquid hourly space velocity of the liquid through the alkylation zone may likewise be varied over a relatively wide range of from about 0.1 to about 20 or more.

In the prior art processes for the production of an alkylaromatic hydrocarbon, for example, dodecylbenzene, the unreacted benzene is recycled as a portion of the feed to the alkylation reaction zone. To accomplish this, the alkylation product effluent, at least the normally liquid hydrocarbon portion thereof, must be separated in a first fractionating column to provide a benzene-rich overhead fraction for recycle to the alkylation reactor, and a bottoms fraction containing materials of intermediate boiling range (for example, paraffins and unreacted olefins), and the desired alkylate product. This bottoms stream must be further fractionated to separate the intermediate fractions as an overhead product, recovering the alkylate as a bottoms product substantially free from benzene. This involved separation technique is contrasted with that permitted through the use of the combination process of the present invention wherein a single fractionator will suffice to permit recovery of the alkylbenzene product while providing a paraffin-aromatic mixture which is recycled to combine with the paraffin feed to the dehydrogenation reaction zone. Thus, the inventive concept of recycling the unreacted aromatic hydrocarbons to the dehydrogenation section offers advantages with respect to both the alkylation section and the dehydrogenation section. With respect to the latter, and as hereinafter indicated in a specific example, conversion, selectivity of conversion and dehydrogenation stability are improved whereas, with respect to the former, significant economic advantages arise as a result of the simplified method for recovering the alkylaromatic product. Furthermore, as a

result of the preferred operating conditions imposed upon the dehydrogenation reaction zone, and the utilization therein of a preferred catalytic composite hereinbefore set forth, any unreacted mono-olefinic hydrocarbons contained within the benzene-paraffin recycle stream, will pass unchanged through the dehydrogenation reaction zone. Other advantages attendant upon this combination process will be readily recognized by those possessing skills in the art of chemical processing techniques.

The following examples are presented for the sole purpose of further illustrating the combination process of the present invention and the advantages to be afforded through the utilization thereof. It is not intended that the operating conditions, charge stock, catalyst, rates, etc., shall be limited upon the scope of the present invention as defined in the appended claims.

The catalytic composite utilized in the dehydrogenation section was disposed in a stainless-steel tube of 7/8-inch nominal inside diameter. The catalyst was disposed therein in amounts ranging from about 5.0 cc. to about 30.0 cc., above which was placed approximately 11.0 cc. to about 30.0 cc. of alpha-alumina particles. The heat of reaction was supplied by an inner spiral preheater located above the alpha-alumina ceramic particles. A commercially available alumina carrier was impregnated with chloroplatinic acid and lithium nitrate to yield a finished catalyst containing about 0.75% by weight of platinum and 0.50% by weight of lithium. When this catalytic composite was "doped" with an attenuator, for example, arsenic, an ammoniacal solution of As_2O_5 was utilized in the quantity required to give the desired atomic ratio of arsenic to platinum. The incorporation of the arsenic component was made by impregnating the lithiated alumina-platinum composite, followed by drying at a temperature of about 210° F. and calcination in a muffle furnace for approximately two hours at a temperature of 932° F. Previous work in the dehydrogenation of paraffinic hydrocarbons, and especially the longer chain paraffinic hydrocarbons, containing from about 10 to about 20 carbon atoms per molecule, has resulted in the preference for lithiated-alumina, arsenic-attenuated platinum catalyst, and in the preferred ranges of dehydrogenation conditions as hereinbefore set forth. Thus, where two catalysts were prepared, both containing arsenic, but one void of lithium or other alkalizing agent, the latter, at identical operating conditions, resulted in a conversion of normal undecane of 15.7% accompanied by a selectivity to the desired mono-olefin of 77.1%. With the catalyst containing lithium, in addition to the arsenic, the conversion increased to 21.4% while the selectivity increased to 84.1%. Where both catalysts contained lithium, but one catalyst was devoid of arsenic or other catalytic attenuator, the addition of arsenic increased the conversion 4.7% based upon the paraffin feed, while the selectivity of conversion remained substantially the same. In another instance, wherein the purpose was to determine the stabilizing effect exhibited by the attenuating component, the results after 110 hours of operation, without arsenic on the catalyst, indicated a conversion of 5.8%, down from an initial conversion of 8.2%. Utilizing the arsenic-attenuated catalyst, the initial conversion was 7.8%, while the conversion at the end of 115 hours was 12.5%. During both operations, the temperature was at an initial level of 426° C., being increased to a level of 477° C. at about 105 hours.

Example I

For both operations hereindescribed, the catalytic composite, having an apparent bulk density of 0.4 gram per cc., was a composite of alumina, 0.75% by weight of platinum, 0.50% by weight of lithium and arsenic in an atomic ratio to platinum of 0.3. The operating conditions included a temperature of 850° F., a liquid hourly space velocity of 32, an operating pressure of 15.0 p.s.i.g. and a hydrogen to hydrocarbon mol ratio of 8.0. Without the

addition of benzene to the normal dodecane charge stock, the conversion was 10.7% and the selectivity thereof to the desired monoolefin was 93.3%. During a second operation, benzene was added in an amount of about 35% by weight, such that the mol ratio of benzene to normal dodecane was 1.175 to 1. Under the same severity of operating conditions, the percent conversion increased to 11.5, accompanied by a selectivity of conversion to the mono-olefin of 96.6%.

Example II

In addition to the benefits resulting from the increased conversion and efficiency of conversion, the benzene dilution of the paraffin feed imparts a significant degree of stability to the entire operation. This is indicated in this example wherein the charge stock was normal dodecane and the operating conditions included a pressure of 15 pounds per square inch, a liquid hourly space velocity of 32 and a hydrogen to hydrocarbon mol ratio of 8.0. For the first 15 hours of operation, the temperature was maintained at 825° F., and subsequently increased to a temperature of 850° F. for the remainder of the operation. Periodic samples were obtained for the purpose of determining the percent of conversion of the normal dodecane and the selectivity thereof to the desired normal dodecene. For the operation involving benzene dilution, benzene was added to the normal dodecane charge stock in an amount such that the mol ratio of benzene to dodecane was controlled at a level of 1.175 to 1. The results with respect to conversion are indicated in the following Table I, and are those obtained at the end of the time period.

TABLE I.—STABILITY EFFECT OF BENZENE

Time in hours	Conversion, Percent	
	No benzene dilution	Benzene dilution
20	12.0	10.5
25	11.5	10.9
30	11.2	11.2
40	10.7	11.5
50	10.4	11.6
60	10.3	11.7
70	10.2	11.7
80	10.1	11.7
90	10.0	11.7

The stability with respect to conversion of normal dodecene is evident upon reference to the foregoing tabulated data. It might be added that the efficiency of conversion, in the absence of benzene dilution and at the end of the initial 15 hours, during which time the temperature was at a level of 825° F., was 93.8. This is contrasted to the efficiency of conversion obtained during the first 15 hours with respect to the benzene-diluted operation, which efficiency was virtually 100.0% as a result of only trace quantities of di-olefins in the product effluent. With respect to that portion of the operation effected at a temperature of 850° F., after 25 hours using benzene, the efficiency of conversion was 98.7 as contrasted to the 91.4 in the absence of benzene. A composite sample obtained during the 90–95 hour portion of the operation, with benzene dilution, indicated a selectivity of 97.8%. This in turn was contrasted to an efficiency of conversion of 94.1% obtained in the absence of benzene dilution, on a composite sample taken during the 81–87 hour portion of the operation.

Example III

This example is presented for the primary purpose of illustrating the applicability of the present combination process to a commercial size unit having available a Middle-East crude oil as the charge stock source. Significant quantities of normal paraffins having from 11 to 18 carbon atoms per molecule are contained in this crude, and the desired object is to produce a detergent alkylate product (mixed) in which the alkyl groups are in the C₁₁ to C₁₄ range, the C₁₅ to C₁₈ normal paraffins being separately recovered for another purpose.

Following the initial fractionation, treating and separation of the crude oil, 35,440 lbs./hr. of mixed C₁₁ to C₁₉ paraffins are recovered (C₁₉ being in very small quantity). Of this amount, 17,940 lbs./hr. are in the C₁₅ to C₁₉ range, including isoparaffins and aromatics; the remaining 17,500 lbs./hr. constitute a dehydrogenation charge stock having the following composition:

TABLE II

Component:	Concentration, wt. percent
C ₁₁	25.8
C ₁₂	23.6
C ₁₃	23.3
C ₁₄	23.9
Isoparaffins and aromatics	3.4

The dehydrogenation reaction zone contains a catalyst of alumina, 0.75% by weight of platinum, 0.5% by weight of lithium and arsenic in an atomic ratio to platinum of 0.3. Operating conditions are selected to provide a conversion per pass of 12.0% and a selectivity of conversion to the desired mono-olefins of about 95.0%. These operating conditions include a liquid hourly space velocity of 32.0, a hydrogen/hydrocarbon mol ratio of 8.0, a pressure of 15.0 p.s.i.g. and a catalyst bed temperature of 850° F.

The fresh normal paraffin concentrate, including the isoparaffins and aromatic hydrocarbons, in the amount of 3,220 lbs./hr. is admixed with 23,280 lbs./hr. of recycled paraffin concentrate and 12,500 lbs./hr. of benzene, for a mol ratio of benzene to combined feed paraffin of about 1.06:1. Under these operating conditions, the dehydrogenation product effluent, following separation and recycle of a hydrogen-rich gaseous phase (of which about 40 lbs./hr. is removed via pressure control means) has the following composition:

TABLE III

Component:	Quantity, lbs./hr.
C ₁₁ –C ₁₄ paraffins	23,280
Benzene	12,500
Isoparaffins and aromatics	110
Di-olefins	150
C ₁₁ -olefins	780
C ₁₂ -olefins	710
C ₁₃ -olefins	710
C ₁₄ -olefins	720

Discounting the isoparaffins and aromatics originally present in the fresh feed, which are assumed unaffected, the selectivity of conversion to C₁₁–C₁₄ mono-olefins is seen to be 94.1%, or 2,920 lbs./hr. out of a fresh charge consumption of 3,110 lbs./hr.

The liquid effluent from the dehydrogenation zone is admixed with 1,400 lbs./hr. of additional benzene in order to provide an alkylation charge stock in which the benzene/olefin mol ratio is of the order of 10:1. Hydrogen fluoride is added in an amount to provide an HF/hydrocarbon (excluding the normal paraffins) volume ratio of about 1.5:1, and the mixture is passed into an alkylation reaction zone at a temperature of about 100° F. and under a pressure of about 250 p.s.i.g. The space time in the alkylation reactor is slightly less than about fifteen minutes.

The hydrocarbon portion of the alkylation product effluent is separated from the hydrogen fluoride catalyst by washing and stripping, and is passed into a fractionating column being maintained and controlled at conditions which provide a substantially alkylaromatic-free overhead fraction comprising 12,500 lbs./hr. of non-alkylated benzene and 23,280 lbs./hr. of normal paraffins in the C₁₁–C₁₄ range. This overhead fraction is recycled and combined with 3,220 lbs./hr. of fresh feed to the dehydrogenation reaction zone. The bottoms fraction is introduced into a second fractionating column which is controlled and maintained to separate a heavy alkylate

bottoms fraction and a detergent alkylate overhead product fraction. Of this bottoms fraction, 750 lbs./hr. is heavy alkylate and 20 lbs./hr. is polymer resulting from olefin-polymerization in the alkylation reaction zone. The remainder, being the desired alkylbenzene product, in an amount of 3,810 lbs./hr. has the following composition:

TABLE IV

Component:	Quantity, wt. percent
C ₁₁ -alkylate -----	27.7
C ₁₂ -alkylate -----	24.6
C ₁₃ -alkylate -----	23.8
C ₁₄ -alkylate -----	23.9

The molecular weight of the alkylate product is about 251 and the specific gravity is 0.854.

With reference once again to the drawing, it is understood that the vessel shown as fractionator 18 may, in the actual practice of my invention, in fact be a more complex fractionation system. In illustration, for example, when the alkylation section is the well known HF alkylation process, it will be recognized by those skilled in the petroleum refining art, that the following separations are necessarily made: (1) a hydrofluoric acid stream, containing a minor quantity of benzene, will be separated and recycled to the alkylation reaction zone; (2) a benzene-paraffin stream, substantially free from acid, is separated and recycled to the dehydrogenation reaction zone; and, (3) the alkylbenzene product is withdrawn to storage. However, it is not believed essential, for a complete understanding of my invention to encumber the drawing in this regard, particularly since no claim is herein made to the HF alkylation process other than as directed toward the combination thereof with the dehydrogenation process.

The foregoing examples and specification clearly illustrate the method by which the combination process of the present invention is conducted and the benefits to be afforded through the utilization thereof. Through the expediency of recycling the unreacted benzene, from the alkylation product, to combine with the dehydrogenation charge, the separation facilities for recovering the alkylate product have been simplified, and the dehydrogenation results enhanced considerably.

I claim as my invention:

1. A process for the production of an alkyl-aromatic hydrocarbon which comprises the steps of:

- (a) dehydrogenating a paraffinic hydrocarbon in a catalytic dehydrogenation reaction zone under dehydrogenation conditions and in the presence of hydrogen and a recycled, unreacted aromatic hydrocarbon obtained from an alkylation product effluent as hereinafter set forth;
- (b) separating a hydrogen-rich gaseous phase from the resulting dehydrogenation product effluent and passing the remainder of said effluent, including unreacted paraffinic hydrocarbon and said aromatic hydrocarbon into an alkylation reaction zone maintained under alkylation conditions and in contact with an acid-acting alkylation catalyst;
- (c) separating the resulting alkylation product effluent

to provide a mixture of said paraffinic hydrocarbon and unreacted aromatic hydrocarbon, recycling said mixture to said dehydrogenation zone, and recovering an alkyl-aromatic hydrocarbon product.

2. The process of claim 1 further characterized in that said aromatic hydrocarbon is a mono-nuclear aromatic hydrocarbon.

3. The process of claim 1 further characterized in that said paraffinic hydrocarbon is a normal paraffin containing from 3 to about 20 carbon atoms per molecule.

4. The process of claim 1 further characterized in that said dehydrogenating conditions include a temperature above about 750° F., a pressure of at least about 10 p.s.i.g. and a liquid hourly space velocity above about 10.

5. The process of claim 1 further characterized in that said alkylation catalyst is hydrogen fluoride.

6. The process of claim 1 further characterized in that said alkylation catalyst is boron halide.

7. A process for the production of a mono-nuclear alkylaromatic hydrocarbon which comprises the steps of:

- (a) dehydrogenating a normal paraffinic hydrocarbon containing from about 10 to about 15 carbon atoms per molecule in contact with a noble metal-containing catalytic composite disposed in a dehydrogenating reaction zone under dehydrogenation conditions and in the presence of hydrogen and a recycled, unreacted mono-nuclear aromatic hydrocarbon, obtained from an alkylation product effluent as hereinafter set forth, the latter present in a mol ratio to said normal paraffin of from about 0.5:1 to about 2:1,

- (b) separating a hydrogen-rich gaseous phase from the resulting dehydrogenation product effluent and passing the remainder of said effluent, including unreacted normal paraffinic hydrocarbon and said mono-nuclear aromatic hydrocarbon into a hydrogen fluoride catalyzed alkylation reaction zone, maintained under alkylation conditions;

- (c) treating the resulting alkylation product effluent to recover a substantially hydrogen fluoride-free hydrocarbon mixture;

- (d) separating said mixture to provide a hydrocarbon stream rich in unreacted aromatic hydrocarbon and said normal paraffin, recycling said stream to said dehydrogenation reaction zone, and recovering a mono-nuclear alkylaromatic hydrocarbon.

8. The process of claim 7 further characterized in that said mono-nuclear aromatic hydrocarbon is benzene.

9. The process of claim 7 further characterized in that said normal paraffin contains from 11 to 14 carbon atoms per molecule.

10. The process of claim 7 characterized in that said noble metal catalyst contains platinum.

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