

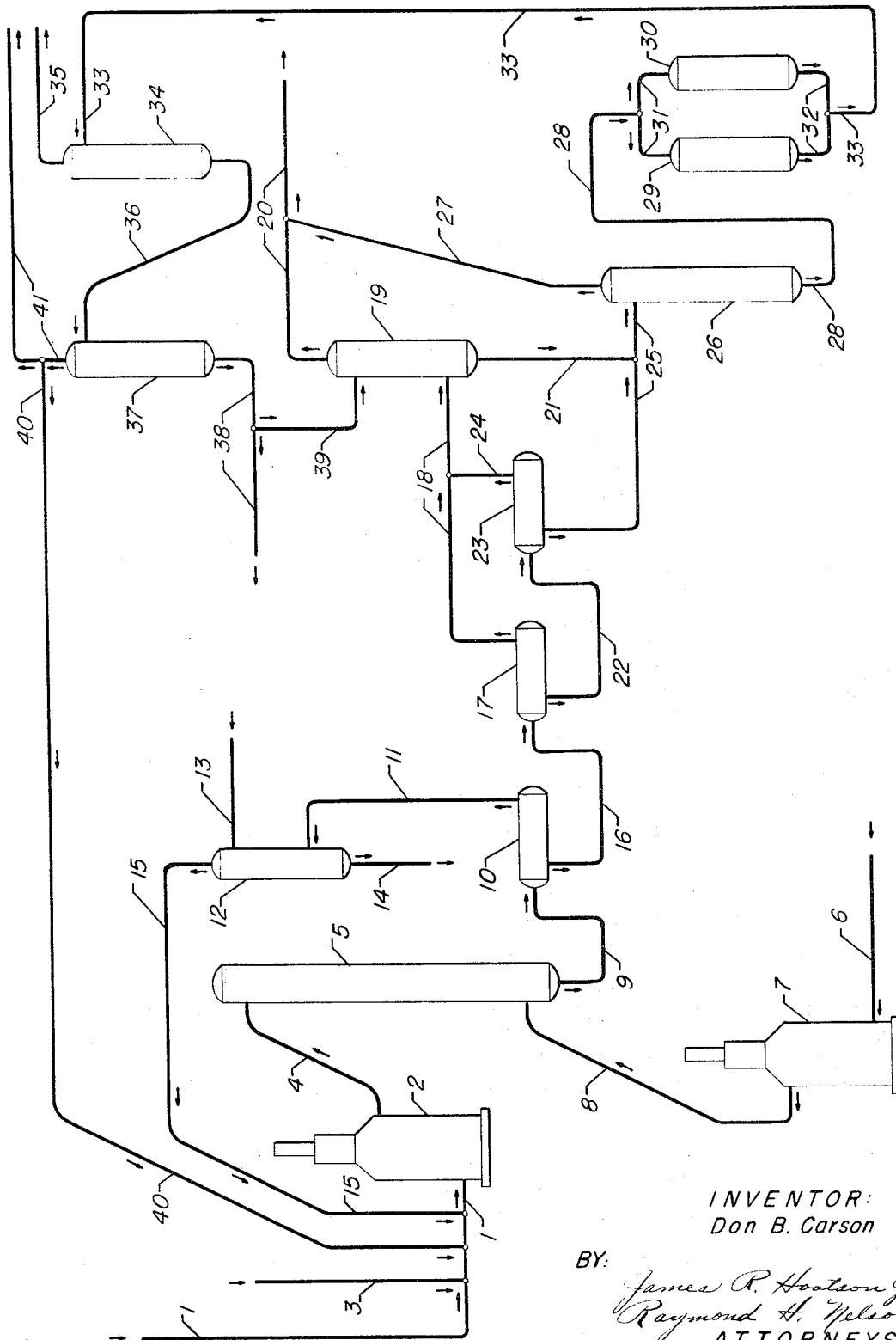
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HYDRODEALKYLATION OF ALKYL AROMATIC HYDROCARBONS

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HYDRODEALKYLATION OF ALKYL AROMATIC
HYDROCARBONS

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This invention relates to a process for the hydrodealkylation of alkyl aromatic hydrocarbons. More specifically, the invention is concerned with a process for the hydrodealkylation of alkyl aromatic hydrocarbons in which the purity of the hydrogen which is recycled during the process is greatly improved.

In recent years, the necessity or need for a high grade, pure benzene has increased an appreciable amount. For example, benzene having a high technical grade purity is an important starting material for the production of alkyl aromatic sulfonates which are useful as detergents and surface active agents. The alkyl aromatic sulfonates are prepared by alkylating benzene with a long chain polymer containing from about 12 to about 15 carbon atoms or more in the chain said polymer having been generally prepared by polymerizing propylene or butene. After the benzene has been alkylated the resultant compound may be sulfonated by any method well known in the art to produce the corresponding sulfonic acids. These acids may then be neutralized by any basic material such as sodium hydroxide, potassium hydroxide, etc., to form the corresponding sulfonates such as the sodium or potassium salt of the alkylaryl sulfonic acid. In addition to the aforementioned use of a relatively pure aromatic hydrocarbon such as benzene, as also in some instances naphthalene, as intermediates in the preparation of detergents, the high grade, relatively pure aromatic hydrocarbons may also find uses as intermediates in the preparation of many organic compounds such as insecticides, pharmaceuticals, resins, dyes, perfumes, etc. While it is admitted that alkyl aromatic compounds such as toluene, ortho-xylene, meta-xylene, para-xylene, ethylbenzene, methyl-naphthalene, dimethylnaphthalene, etc., may also be useful in the preparation of chemical compounds this invention is concerned mainly with the production of unsubstituted aromatic hydrocarbons. The feed stocks for the process of this invention may be obtained from many sources, for example, the by products resulting from the processes utilized in the petroleum industry may contain aromatic hydrocarbons containing one or more alkyl substituents on the ring. Another source of feed stock for the process of this invention is the coal tar industry which finds that after distillation of coal the coal tar crudes contain a mixture of benzene, toluene, xylenes, naphthalene, etc. After the coal tar is recycled the hydrocarbons present are separated from each other by fractional distillation, the toluene, xylenes, methylnaphthalenes, etc., which are recovered may then be hydrodealkylated according to the process of the present invention to provide a greater yield of the desired products which, in the instance, comprises benzene, naphthalene, etc.

According to the process of the present invention, the hydrodealkylation of the alkyl aromatic compounds is effected in the presence of an excess of hydrogen, and if so desired, a catalytic composition of matter, more fully described hereinafter, at hydrodealkylation conditions which include elevated temperatures and pressures. When utilizing toluene and the xylenes or methylnaphthalene as a charge stock, the principal reaction is, of course, demethylation of the substituents on the aromatic ring to form benzene or naphthalene plus methane. This reaction is strongly exothermic, the rate of demethylation increasing slowly with an increase in temperature, how-

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ever, the temperature must of necessity be controlled within a desired range in order to remove a large amount of reaction heat which might build up and have a tendency to destroy the desired product by hydrocracking the aromatic ring to form carbon.

The present invention is specifically concerned with an improvement in a process for dealkylating alkyl aromatic hydrocarbons in the presence of hydrogen and, if so desired, a hydrodealkylation catalyst, by utilizing certain improvements in the process whereby side reactions will be minimized and a lesser amount of make-up hydrogen is required due to a higher degree of hydrogen purity in the recycle stream. While the principal reaction in the hydrodealkylation of alkyl aromatic hydrocarbons is the elimination of the alkyl groups from the aromatic nucleus, two side reactions may also occur. These side reactions are the decomposition of some of the aromatic nuclei to form light paraffins and the condensation of mononuclear aromatic hydrocarbons to polynuclear aromatic hydrocarbons. However, if the process is properly operated, the side reactions are held to a minimum and the ultimate product of aromatic hydrocarbons and light hydrocarbons may be over 90%.

If the feed stock also contains non-aromatic hydrocarbons as well as alkyl aromatic hydrocarbons, the former, under the conditions of the process may also be decomposed to light paraffins, principally methane, and therefore the process will produce an aromatic hydrocarbon such as benzene of high purity even though the charge stock contains paraffins which normally have a boiling range approximately the same as benzene. Along with the controlled temperatures and pressures of the type hereinafter set forth in greater detail, which control the formation of undesired side products, it is necessary to operate the process so as to eliminate the decomposition of methane which is formed during the reaction to free carbon. If this reaction is allowed to occur, massive carbon formation will result and free carbon will be deposited on the walls of the reactor and other pieces of apparatus, in the spaces surrounding the catalyst as well as on the catalyst particles, thereby rendering the catalyst inoperative and necessitating frequent shutdowns for decoking of the catalyst or changing the catalyst entirely.

It is therefore an object of this invention to provide an improved process for the production of aromatic hydrocarbons by hydrodealkylating alkyl aromatic hydrocarbons.

A further object of this invention is to provide an improved method for the production of aromatic hydrocarbons by the hydrodealkylation of alkyl aromatic hydrocarbon whereby the net hydrogen consumption is greatly reduced with a correspondingly smaller amount of make-up hydrogen being required.

In a broad aspect, one embodiment of this invention resides in a process for the hydrodealkylation of an alkyl aromatic hydrocarbon which comprises passing said hydrocarbon to a reaction zone, treating said hydrocarbon with added hydrogen at hydrodealkylation conditions, passing the reaction mixture to a first separation zone, separating said mixture into a hydrogen-rich gaseous phase and a liquid hydrocarbon phase, recycling said gaseous phase to combine with said alkyl aromatic hydrocarbon, passing said liquid hydrocarbon phase to a second separation zone, separating light hydrocarbons from said liquid hydrocarbon phase and recovering the desired product from the liquid hydrocarbon phase from said separation zone, the improvement of said process comprising treating said reaction mixture with steam in the presence of a steam-methane reforming catalyst prior to entry of said mixture into said first separation zone.

A further embodiment of this invention is found in a process for the hydrodealkylation of an alkyl aromatic

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hydrocarbon which comprises passing said hydrocarbon to a reaction zone, treating said hydrocarbon with added hydrogen in the presence of a hydrodealkylation catalyst at a temperature in the range of from about 1000° to about 1500° F. and at a pressure in the range of from about 300 to about 1000 pounds per square inch, passing the reaction mixture to a first separation zone, separating said mixture into a hydrogen-rich gaseous phase and a liquid hydrocarbon phase, recycling said gaseous phase to combine with said alkyl aromatic hydrocarbon, passing said liquid hydrocarbon phase to a second separation zone, separating light hydrocarbons from said liquid hydrocarbon phase, and recovering the desired product from said liquid hydrocarbon phase from said second separation zone, the improvement of said process comprising treating said reaction mixture with steam in the presence of a steam-methane reforming catalyst at the outlet end of said reaction zone prior to discharge of said mixture therefrom.

Other objects and embodiments will be found in the following further detailed description of this invention.

As hereinbefore set forth, the present invention is concerned with an improvement in a process for the hydrodealkylation of alkyl aromatic hydrocarbons whereby the purity of the hydrogen which is recycled to the reaction zone is greatly improved, and the net consumption of the hydrogen in the process is decreased. The ratio of hydrogen to ethane and lighter hydrocarbons such as methane in the reactor effluent should be at least 60 mole percent in order to prevent carbon formation. There are two alternatives to maintain this ratio: (1) sufficient make-up hydrogen can be brought into the reaction stream to satisfy both the chemical hydrogen consumption and that required to give the aforementioned 60 mole percent hydrogen:hydrocarbon ratio in the reactor effluent or (2) supply a lesser quantity of hydrogen make-up gas and utilize a hydrogen-enrichment or purification scheme to increase the utilization of the hydrogen feed gas. By utilizing such a scheme, that is the hydrogen-enrichment plan of the present process, the cost of the operation is greatly decreased inasmuch as a lesser amount of make-up hydrogen is required, thus rendering the process more commercially attractive to operate.

In a simplified version, the hydrodealkylation process is effected by charging an alkyl aromatic hydrocarbon and added hydrogen to a reaction zone which is maintained at hydrodealkylation conditions comprising a temperature in the range of from about 1000° to about 1500° F. and at a pressure in the range of from about 300 to about 1000 pounds per square inch, the feed stock being charged at a liquid hourly space velocity in a range of from about 0.1 to about 20 and at a preferred range of from about 0.5 to about 5. In addition, the hydrogen:hydrocarbon ratio should be in the range of from about 5:1 to about 50:1. If so desired, the hydrodealkylation may be effected in a thermal manner or in the presence of a hydrodealkylation catalyst of the type hereinafter set forth in greater detail.

The reaction mixture is withdrawn from the reaction zone and passed to a high pressure separator which is maintained at a pressure in the range of from about 250 to about 1000 pounds per square inch wherein the mixture is separated into a hydrogen-rich gas fraction and a liquid hydrocarbon fraction. The present invention is concerned with an improvement in this process whereby the reaction mixture is contacted with steam in the presence of a steam-methane reforming catalyst. The term "steam-methane reforming catalyst" as used in the present specification and appended claims will refer to catalysts which are capable of converting the methane in the reactor effluent which is present from the demethylation to hydrogen and carbon oxides. These catalysts preferably comprise a metal or metal compound of Group VIII of the Periodic Table composited on a solid carrier. Other metals which may be utilized include chromium, man-

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ganese, copper, molybdenum, vanadium, tungsten, and mixtures thereof. The solid carrier base upon which the metal is composited may include alumina, zirconia, magnesia, silica, silica-alumina, etc., the preferred support comprising alumina. The metal, metal compound or mixtures thereof are present on the carrier base in an amount ranging from about 5 to about 30% by weight of catalyst composite. Specific examples of these catalysts include 20% by weight of nickel composited on alumina, 27% by weight of nickel composited on alumina, 23% to 35% by weight of nickel oxide composited on alumina, 20% by weight of chromia composited on alumina, etc.

By treating the reaction mixture with super-heated steam in the presence of a steam-methane reforming catalyst in the hydrodealkylation zone the necessity for utilizing a recycle stream as a quench is eliminated. Inasmuch as the overall reaction of hydrodealkylation, a specific illustration being the demethylation of toluene to form benzene and methane, is believed to involve several free radical steps and is strongly exothermic in nature, care must be taken to introduce some means whereby the temperature in the reaction zone is controlled within a predetermined range. If the temperature is allowed to rise into what may be designated as an unsafe range there will be a tendency for the methane to decompose into carbon and hydrogen with the resultant deposit of free carbon in the system. In addition, inasmuch as the process is effected at temperatures in the range of from about 1000° to about 1500° F. or more, certain care must be used in determining what material will be utilized for the reactor, the pipelines, the heaters, pumps, etc. If the reactor effluent which is discharged from the reaction zone leaves at too high a temperature, the pieces of apparatus which are required must therefore, of necessity, consist of high temperature resistant alloys which will raise the cost of the unit whereby the economic operation of said unit will be seriously impaired. The treatment of the reaction mixture with steam in the presence of a catalyst of the type hereinbefore set forth in greater detail is strongly endothermic in nature and therefore this treatment will act as a quench whereby the temperature of the reaction mixture leaving the hydrodealkylation zone will be greatly reduced and will be within the desired limit.

Following the separation of the reaction mixture in the high pressure separator into a hydrogen-rich gas fraction and a liquid hydrocarbon fraction the former is recycled to the reaction zone. In the present process, the hydrogen-rich gas fraction is passed through an absorber wherein the carbon dioxide and/or carbon monoxide, which has formed from methane being passed over a steam-methane reforming catalyst in the presence of steam, is removed utilizing an organic compound as a solvent therefor. Inasmuch as hydrogen has been produced in the reactor through the reaction of steam with the methane in the presence of a steam-methane reforming catalyst, the system will require less make-up hydrogen to be added to the feed stream before entry into the hydrodealkylation zone.

The liquid hydrocarbon fraction may then, if so desired, be charged to an intermediate pressure separator which is maintained at a pressure in the range of from about 50 to 150 pounds per square inch. Subsequently, the liquid hydrocarbon fraction may be charged to a low pressure separator which is maintained at approximately atmospheric pressure. In the intermediate pressure separator and low pressure separator any light hydrocarbons which may still be present will flash up and pass to a gas absorber, wherein the light hydrocarbons are separated from any aromatic hydrocarbon or alkyl aromatic hydrocarbon which may be present, and utilized as fuel. The liquid hydrocarbon fraction is then passed to clay treaters for purification and thence to fractionators whereby the desired aromatic hydrocarbons are separated and recovered, any unreacted alkyl aromatic hydrocarbons also

being recovered and recycled back to form a portion of the feed stock.

The present invention will be further illustrated with reference to the accompanying drawing which is a simplified diagrammatic flow diagram of one embodiment of the process. It is to be understood that the drawing, as well as the explanation thereof, is given for the purpose of illustration and is not intended to limit the process of the present invention to the particular flow so illustrated. For the sake of a simplification and clarity, various valves, heaters, condensers and other appurtenances have been eliminated from the drawing, only vessels and connecting lines which are necessary for a complete understanding of the process are herein indicated.

Referring now to the drawing, a feed stock comprising an alkyl aromatic hydrocarbon which may, if so desired, have undergone pretreatment whereby any undesirable contaminants such as olefins, sulfurous compounds, nitrogenous compounds, or oxygen-containing compounds have been removed, is charged through line 1 to a heater 2 wherein the charge is heated to the desired reaction temperature. In addition, any make-up hydrogen which is required is added through line 3 to the charge stock prior to entry to heater 2. After being heated to the desired reaction temperature the charge is withdrawn from heater 2 through line 4 and passed to a hydrodealkylation reaction zone 5. This reactor may, if so desired, contain a hydrodealkylation catalyst of the type hereinafter set forth in greater detail. In hydrodealkylation reaction zone 5 the alkyl aromatic hydrocarbons undergo hydrodealkylation in the presence of the added hydrogen. In addition, hydrodealkylation reaction zone 5 also contains a steam-methane reforming catalyst bed at or near the outlet end thereof. The reaction mixture passes in a down-flow through this catalyst bed wherein it is treated with super-heated steam which is charged through line 6 to a heater 7 wherein it is heated to the desired temperature and thence through line 8 to zone 5. Following the treatment of the reaction mixture with steam the reaction mixture is withdrawn from hydrodealkylation zone 5 through line 9 and passed to high pressure separator 10. As hereinbefore set forth, the high pressure separator or flash drum will be maintained at a pressure in the range of 250 to about 1000 pounds per square inch. In separator 10 the reaction mixture is separated into a hydrogen-rich gaseous phase and a liquid hydrocarbon phase. The hydrogen-rich gaseous phase is withdrawn through line 11 to an absorber 12. In absorber 12 the carbon monoxide and/or carbon dioxide is dissolved in a suitable solvent such as monoethanolamine or diethanolamine, etc. which is added to absorber 12 through line 13 and is withdrawn through line 14 while the enriched hydrogen is recycled through line 15 to admix with the alkyl aromatic feed in line 1 prior to entry into heater 2.

The liquid hydrocarbon phase is withdrawn from high pressure separator 10 through line 16 and charged to an intermediate pressure separator or flash drum 17. This second separator or flash drum is maintained at a lower pressure than is found in the first separator, the pressure usually being in the range of from about 50 to 150 pounds per square inch. In this second separator the light gaseous hydrocarbons are withdrawn and passed through line 18 to a gas absorber 19. If so desired, the light gaseous hydrocarbons may be recovered and passed through line 20 to storage for subsequent use as fuel. Any desirable aromatic hydrocarbons or unreacted alkyl aromatic hydrocarbons which may have been contained in the gas entering absorber 19 are withdrawn through line 21. The light hydrocarbon fraction which is separated from the aforementioned light gaseous hydrocarbon in intermediate gas separator 17 is withdrawn through line 22 and passed to a low pressure separator 23. This low pressure separator is maintained at approximately atmospheric pressure. In low pressure separator 23, any

gaseous hydrocarbons which may still be present are separated and withdrawn through line 24 where they are admixed with the gaseous products in line 18 before said gaseous products pass into absorber 19. The liquid hydrocarbon fraction which remains is withdrawn from low pressure separator 23 through line 25 and passed to stripper 26. In stripper 26, any gaseous hydrocarbon which may still be entrained in the liquid hydrocarbon fraction after passing said fraction through the individual separators are stripped and withdrawn through line 27 where they are admixed with the light gaseous hydrocarbons which were withdrawn from gas absorber 19 through line 20. The stripped liquid hydrocarbon fraction is withdrawn from stripper 26 through line 28 and passed to clay treaters 29 and 30 through line 31. In clay treaters or towers 29 and 30 the liquid hydrocarbon fraction is treated to remove any impurities in order that the aromatic hydrocarbons, either monocyclic or polycyclic in nature will meet acid wash color and bromine index specifications. The treated fraction is withdrawn from the clay treaters 29 and 30 through line 32 and passed through line 33 to a fractionating tower 34 wherein the desired aromatic hydrocarbon, either monocyclic or polycyclic in nature, are separated. The desired aromatic hydrocarbons are withdrawn through line 35 and passed to storage. Any unreacted alkyl aromatic hydrocarbons are withdrawn as bottoms from fractionator 34 through line 36 and passed to a second fractionation zone 37. The heavy aromatic bottoms are withdrawn from fractionation zone 37 through line 38, a portion of said heavy aromatics being recycled, if so desired, to absorber 19 by means of line 39, whereby said heavy aromatics can function as a solvent or absorbing agent for the liquid gaseous hydrocarbons. The unreacted alkyl aromatic hydrocarbons such as toluene, xylene, methylnaphthalene, etc. are withdrawn overhead through line 40, a portion of said overhead being utilized as recycle liquid being passed through line 40 for admixture with the feed stock in line 1 prior to passage in heater 2, the remainder of the unreacted alkyl aromatic hydrocarbons being withdrawn through line 41 and passed to storage.

It is to be understood that, as hereinbefore set forth, the aforementioned description of the process is only one embodiment and that other variations may be employed without departing from the scope of the invention. For example, the process may be effected by using only two separators or flash drums, the first being a high pressure separator or flash drum which is maintained at a pressure in the range of about 250 to about 1000 pounds per square inch and the second being a low pressure separator or flash drum which is maintained at approximately atmospheric pressure. Another variation which may be employed is to treat the reaction mixture with super-heated steam in a reaction zone subsequent to the removal of the reaction mixture from the hydrodealkylation zone and prior to entry into the high pressure separator. The sensible heat of the reactor effluent will provide the heat of reaction for the treatment of the effluent with steam in the presence of a steam-methane reforming catalyst of the type hereinbefore set forth. It is also contemplated within the scope of this invention that the steam-methane reforming catalyst may be of a similar type of that used in the hydrodealkylation reaction so that the hydrodealkylation reaction zone may comprise a reaction zone containing a series of beds of catalyst or a single bed of catalyst, the super-heated steam being injected in either a lower bed of a series of catalyst or at a lower point in the single bed of catalyst.

The catalyst which is utilized in the hydrodealkylation zone may contain a noble metal of Group VIII of the Periodic Table such as platinum, palladium, rhodium, ruthenium, osmium, or iridium composited on a suitable refractory oxide. In addition the catalyst may contain

other metals such as cesium, vanadium, chromium, tungsten, etc., composited on a suitable refractory oxide. It is also contemplated that combinations of the latter classes of metallic components may be utilized with themselves or with a noble metal of Group VIII of the Periodic Table. Suitable refractory oxides which may be used include alumina, particularly alumina containing a relatively high surface area such as gamma-alumina, eta-alumina and theta-alumina, as well as mixtures of metallic oxides such as silica-zirconia, silica-alumina, alumina-boria, silica-zirconia-alumina, etc. A particularly effective hydrodealkylation catalyst comprises chromia impregnated on high surface area alumina, said metal being present in the finished catalytic composite in an amount of from about 10 to about 20% by weight or more calculated as the elemental metal.

The catalysts which are to be utilized in the hydrodealkylation reaction may be prepared in any manner well known to the art. One such type of preparation is to dry the desired refractory oxide base such as a high surface area alumina in order to reduce the volatile content of said base to a minimum. The dried base is then pilled to a desired crushing strength and calcined at a relatively high temperature of from about 1000° to about 1300° F. Following this, the base is impregnated with the metal in any manner, one such application being to impregnate the base with a solution of a metal such as chromium following which the composite is dried and oxidized at a relatively high temperature of from about 1200° to about 1400° F. for a period of about three hours.

As hereinbefore set forth by utilizing the process of the present invention whereby the reaction mixture is treated with steam in the presence of a steam-methane reforming catalyst of the type hereinbefore set forth, it is possible to eliminate certain recycle streams including (1) a recycle stream from the liquid hydrocarbon fraction withdrawn from the high pressure separator and recycled to the outlet end of the hydrodealkylation zone, said stream acting as a quench to reduce the temperature of the reactor effluent prior to discharge of said effluent from the reaction zone and (2) a recycle stream taken from the liquid hydrocarbon fraction discharged from the low pressure separator and recycled to join the reactor effluent prior to charging said effluent into the first or high pressure separator, said recycle stream acting as a gas absorber to enrich the hydrogen fraction. In addition, it is also possible to enrich the hydrogen recycle stream with a subsequent decrease in the amount of light paraffinic hydrocarbons such as methane or ethane which may be present, thereby minimizing the possibility of catalyst deactivation in the hydrodealkylation zone due to the deposition of coke or other heavy carbonaceous materials upon the catalytically active centers or surfaces of the catalyst. By enriching the hydrogen recycle stream it is possible to reduce the amount of make-up hydrogen which is necessary for the reaction and, in addition, it is also possible according to the process of this invention to produce additional hydrogen which may be utilized therein.

The following example is given to illustrate the process of this invention which, however, is not intended to limit the generally broad scope of the present invention in strict accordance therewith.

Example I

In this example, a feed comprising a coke-oven light oil after being treated to remove contaminants comprising diolefins, sulfurous compounds, nitrogenous compounds and oxygen-containing compounds, is passed to a reactor containing a chromia-alumina catalyst which has been prepared according to the method hereinbefore set forth. The reaction zone is maintained at a pressure of about 550 pounds per square inch and an inlet temperature of 1200° F. In addition, a stream of hydrogen is admixed with the charge as well as a stream of make-up hydrogen

before entering into said reactor, the recycle hydrogen and make-up hydrogen being charged at such a rate so that the hydrogen:hydrocarbon ratio is in a range of from about 5 to about 50. The feed stock will be charged to the reactor at a liquid hourly space velocity which may be defined as a volume of liquid hydrocarbon charge per volume of catalyst per hour in a range of from about 0.1 to about 10 and preferably within a range of from about 0.5 to about 5.0. The feed stock will undergo hydrodealkylation in the reactor by being passed through the catalyst bed.

The reaction mixture is then passed through a second catalyst bed in the reactor wherein it is treated with super-heated steam at the temperature of the reaction mixture which is about 1350° F. A steam-methane reforming catalyst which may be utilized to change the methane into carbon oxides is prepared by drying the alumina at a temperature of about 200° to about 400° F. and forming the dried alumina into particles into definite size and shape. The dried alumina is subjected to calcination at a temperature of at least 900° F. and generally in a range of from 900° F. to about 1500° F., a particularly preferred calcination being from 1100° to 1300° F. to yield a substantially anhydrous alumina. Usually, the calcination is effected in the presence of air or other oxidizing intermediate although in some instances, it may be effected in a reducing atmosphere such as hydrogen or an inert atmosphere such as nitrogen. The time of the calcination will vary with the temperature of the calcination and will generally be from about 0.5 to about 10 hours. Following this, the metallic component of the catalyst which includes the Group VIII metals is then composited with the alumina in any suitable manner. For example, the alumina can be soaked, dipped, suspended or otherwise immersed in a solution of a suitable compound of the selected metal. For example, suitable compounds which may be used include nickel nitrate, nickel sulfate, nickel chloride, cobalt sulfate, cobalt nitrate, ferric chloride, ferric nitrate, platinum chloride, etc. The catalytic composite is then dried at a temperature of from about 200° to about 400° F. and thereafter calcined at a temperature in the range of from about 800° to about 1500° F., preferably at a temperature at about 1100° F. to about 1300° F. The final calcination which may be effected in the presence of air, or other oxidizing atmospheres, reducing atmospheres such as hydrogen, or an inert atmosphere such as nitrogen serves to activate the catalyst component thereof. In any case, the final catalytic composite will contain the metal in an amount of from about 20% to about 30 weight percent thereof computed as the elemental metal.

Due to the endothermicity of the steam treating step, the reactor effluent is withdrawn from the reaction zone at a temperature of about 1150° F. and is passed to a high pressure separator which is maintained in a range of from about 250 to about 1000 pounds per square inch. In this separator, the reactor effluent is separated into a hydrogen-rich gas stream which is flashed off and passed to an absorber wherein the carbon oxides which are formed during the steam treatment are contacted with a solvent comprising diethanolamine and are recovered, the purified hydrogen being recycled to admix with the charge stock prior to entry into the hydrodealkylation reactor. The liquid hydrocarbon bottoms from the high pressure separator are withdrawn and passed to an intermediate pressure separator which is maintained at a pressure in the range of from about 50 to 150 pounds per square inch.

The liquid hydrocarbon mixture is flashed in this separator and the gases containing any light hydrocarbons which remain are passed overhead to a fresh-gas absorber. The liquid hydrocarbon bottoms from this intermediate pressure separator are withdrawn and passed to a low pressure separator which is maintained at atmospheric pressure. In this low pressure separator, any gases still

remaining are flashed off and withdrawn to the fresh-gas absorber where they are admixed with the gases from the intermediate pressure separator. The liquid hydrocarbon bottoms from the low pressure separator are withdrawn and passed to clay treating towers wherein impurities are removed in order that the product pass the acid-wash and bromine index specifications. The liquid stream is then passed to a fractionator wherein fractional distillation is effected. The desired aromatic hydrocarbons, both monocyclic and polycyclic in nature are removed therefrom while the bottoms are charged to a second fractionator. In this second fractionator the high boiling bottoms are removed while any unreacted alkyl aromatic hydrocarbon are recycled to form a portion of the feed stock.

I claim as my invention:

1. A hydrodealkylation process which comprises reacting an alkyl aromatic hydrocarbon with hydrogen at hydrodealkylation conditions, thereby forming a reaction mixture containing dealkylated aromatic hydrocarbon, hydrogen and methane, commingling steam with said mixture and catalytically reacting the same with at least a portion of the methane content of the mixture to convert methane to hydrogen and carbon oxides, separating the resultant hydrogen-enriched reaction mixture into a gaseous phase and a liquid hydrocarbon phase, separating carbon oxides from said gaseous phase to increase the hydrogen concentration of the latter, thereafter supplying the gaseous phase to the aforesaid hydroalkylation step to furnish hydrogen therefor, and recovering the desired dealkylated aromatic hydrocarbon from said liquid phase.

2. The process of claim 1 further characterized in that the hydrodealkylation reaction is catalytic.

3. The process of claim 2 further characterized in that the catalytic hydrodealkylation reaction is performed at a temperature in the range of from about 1000° to about

1500° F. and at a pressure in the range of from about 300 to about 1000 pounds per square inch.

4. A process as set forth in claim 2 further characterized in that the hydrodealkylation catalyst comprises chromia composited on alumina.

5. A process as set forth in claim 1 further characterized in that the catalyst in the steam-methane reaction comprises chromia composited on alumina.

6. A process as set forth in claim 1 further characterized in that the catalyst in the steam-methane reaction comprises a metal of Group VIII of the Periodic Table composited on a solid carrier.

7. A process as set forth in claim 6 further characterized in that said catalyst comprises nickel composited on a solid carrier.

8. A process as set forth in claim 6 further characterized in that said catalyst comprises nickel composited on alumina.

9. A process as set forth in claim 1 further characterized in that said alkyl aromatic hydrocarbon is toluene.

10. A process as set forth in claim 1 further characterized in that said alkyl aromatic hydrocarbon is xylene.

11. A process as set forth in claim 1 further characterized in that said alkyl aromatic hydrocarbon is methyl-naphthalene.

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