

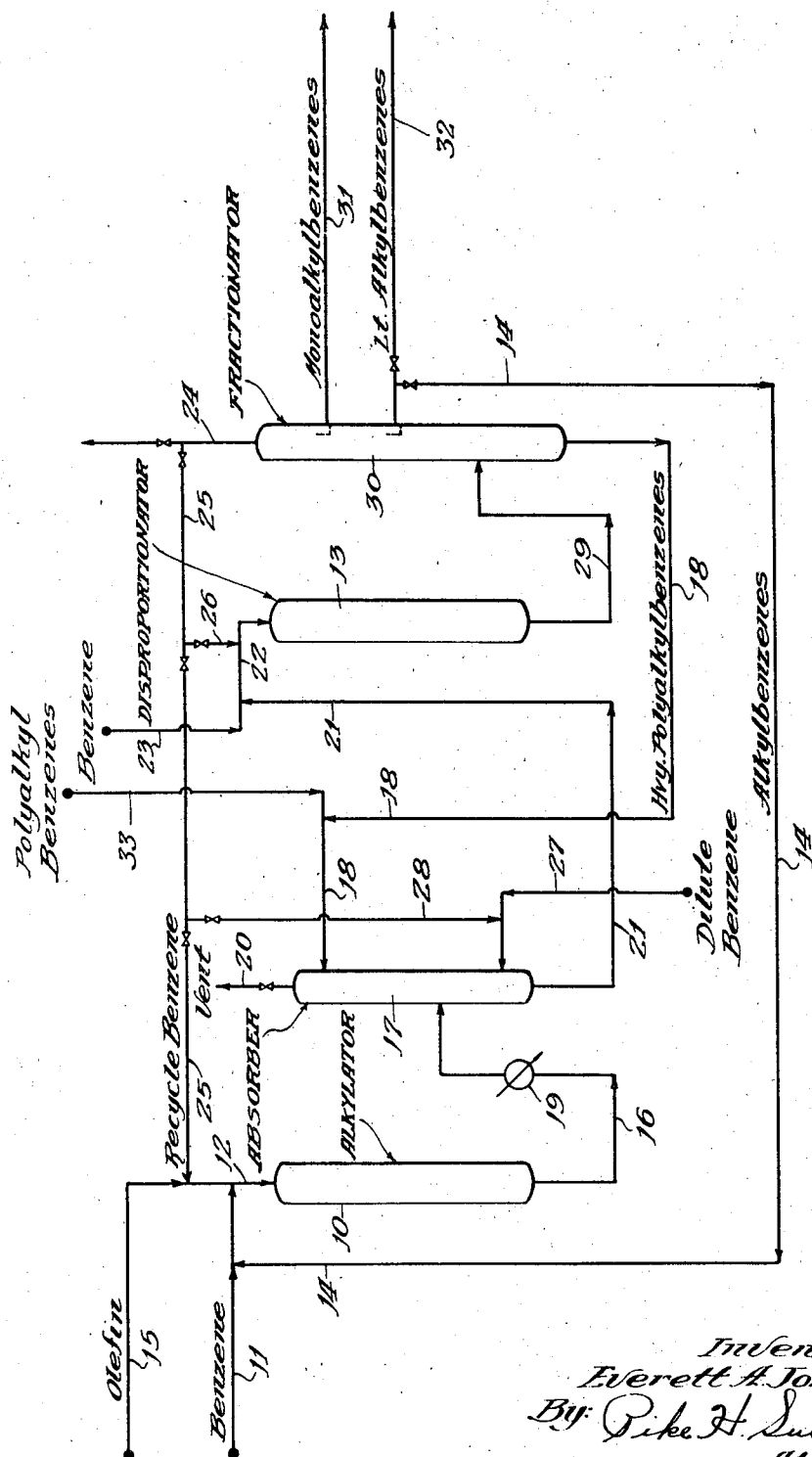
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PRODUCTION OF ALKYLAROMATICS

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PRODUCTION OF ALKYLAROMATICS

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1 This invention relates to the production of alkylaromatic hydrocarbons and relates more particularly to the production of monoalkylbenzenes by the alkylation of benzene with olefins such as ethylene and propylene.

Monoalkylbenzenes and particularly the lower boiling monoalkylbenzenes such as ethylbenzene or isopropylbenzene have been found to be valuable constituents in aviation fuels because of their very high octane number particularly under "supercharged" conditions. In addition valuable products can be prepared therefrom. For example, styrene is produced by thermal or catalytic dehydrogenation of ethylbenzene. The amount present in ordinary refinery streams of petroleum hydrocarbons is comparatively negligible and even in the products from such processes as catalytic or thermal cracking, catalytic aromatization, etc., the ultimate yield of low boiling monoalkylaromatics is comparatively low. Higher boiling aromatics, such as xylene, are obtained in higher yields from such processes but the low octane diluents contained in such fractions are not desirable aviation gasoline constituents.

It has been known for some time that the alkylbenzenes can be synthesized by the alkylation of aromatic hydrocarbons with olefins in the presence of activating catalysts. In such processes it is generally desirable that the charge be rich in benzene and/or olefins because of the great reduction in reaction space, but when an excess of olefins is used, polyalkylbenzenes are formed. Optimum cleanup of benzene from dilute benzene streams by simply alkylating to form the desired monoalkylbenzenes, however, is not the solution since the recycling of unreacted benzene to the alkylation zone is not possible because of the inert diluent.

It is an object of this invention to provide an improved process for the alkylation of aromatic hydrocarbons with olefinic gases to produce optimum proportions of low boiling monoalkylbenzenes. Another object of my invention is to provide an improved process for the production of aviation fuel, including alkylaromatic hydrocarbons, by a combination of integrated steps. A still further object of my invention is to provide an improved process wherein hydrocarbons valuable for aviation fuels are prepared from refinery fuel gases and a benzene-containing fraction. Further objects and advantages will become apparent as the description of my invention proceeds.

Briefly stated my invention contemplates a unitary process including the alkylation of an aro-

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matic hydrocarbon stream with olefins by contacting in the presence of an alkylation catalyst such as phosphoric acid, aluminum chloride hydrocarbon complex, or hydrogen fluoride under alkylation conditions of temperature, pressure and ratio of reactants. Propylene and/or ethylene, for example, may comprise the olefin charge to produce cumene and ethylbenzene and polyisopropyl- and polyethylbenzenes, respectively. The olefin feed may comprise concentrated olefins or dilute fuel gases. The aromatic feed to the alkylation step comprises an alkylbenzene recycle fraction and or benzene. Relatively dilute benzene streams can be used, particularly when concentrated olefins are fed to the alkylation. The alkylbenzene recycle fraction is an intermediate cut from which the desired monoalkylbenzene and a heavy polyalkylbenzene fraction have been separated. The effluent from the alkylation step is introduced into a separator-absorber to which the heavy polyalkylbenzene fraction is supplied as an absorption medium whereby diluent hydrocarbons are removed from the system. A dilute benzene stream may be introduced at a low point in the absorber-separator to scavenge benzene and to purge the diluent hydrocarbons from the dilute stream. The total aromatic stream including the recycled polyalkylbenzenes and the alkylation product is recovered as bottoms from the absorber-separator. This stream comprises essentially polyalkylaromatics and any benzene which was absorbed from any dilute benzene stream. The next step in my unitary process is to subject this predominantly polyalkylbenzene fraction to disproportionation in the presence of added benzene and a quantity of a catalyst similar to that used in the alkylation step, but usually at a higher temperature to produce the desired monoalkylbenzenes by a dealkylation-alkylation. By disproportionation, I refer to the dealkylation of the polyalkylbenzene and the alkylation of the introduced benzene by the alkyl fragments, both reactions tending to produce additional amounts of mono- and of lower boiling polyalkylbenzenes. Ordinarily it will be desirable to recover and recycle a benzene fraction from the disproportionation step. However, in some instances it will be beneficial to introduce the recycle benzene fraction into the initial alkylation zone to produce additional polyalkylbenzenes or into the separator-absorber for recovery of the benzene and the purging of diluent hydrocarbons from the system.

In one embodiment of my invention I employ olefin-benzene mol ratios higher than one in

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order to effect optimum alkylation of the aromatics. Only by using excess olefins can the benzene cleanup exceed about 50%. When 50% of the total benzene is alkylated approximately 75% of the alkylate is monoalkyl- and 25% is polyalkylbenzene. By increasing the olefin to aromatic mol ratio, the cleanup can be increased to 75% under which conditions the alkylate contains about equal amounts of mono- and polyalkylbenzenes. Thus the use of a molar excess of olefins produces substantial amounts of higher boiling polyalkylbenzenes unsuitable for use as a motor or aviation fuel. By my process the lighter of this material is further alkylated, the heavier material is introduced into the separator-absorber at a high point, and the combined streams fed to the disproportionation zone.

The accompanying drawing diagrammatically illustrates apparatus suitable for carrying out one preferred embodiment of my invention and is in the form of a simplified flow diagram.

Referring to the drawing, a benzene stream, for example, such as that derived from naphthas and cycle stocks by thermal or catalytic cracking thereof or preferably by hydroforming naphtha, usually hydroforming straight run naphtha, enters alkylator 10 by lines 11 and 12. The dilute benzene stream may contain between about 10% and about 75% or more benzene. A light polyalkylbenzene fraction recovered from the disproportionator 13 is supplied by line 14 as additional feed and in some instances may comprise substantially the entire aromatic feed to alkylator 10. An olefin, such as propylene, is introduced by line 15 in an amount such as to maintain a mol ratio of olefin to aromatic fed to the alkylator 10 of between about one and about five or higher, for example, above about 2.5. The olefin stream may contain substantial amounts of diluting hydrocarbons such as light paraffins.

The alkylator 10 can be any conventional reactor for contacting hydrocarbons and catalyst and suitably can be a tower containing a bed of supported catalyst, for example, phosphoric acid on kieselguhr. Other forms of catalytic contacting apparatus such as so-called fluid catalyst systems wherein a finely divided solid catalyst is maintained in a highly dispersed phase or in a dense turbulent fluent phase may be used. In the case of hydrogen fluoride or aluminum chloride-hydrocarbon complexes, tower reactors, wherein a pool of catalyst is maintained, can be used. The combined charge is fed at the rate of between 0.01 to 1.0, for example, below about 0.3 gallon per hour per pound of phosphoric acid catalyst within the reactor for maximum olefin and benzene cleanup. Reaction pressure affects the olefin and benzene cleanup and a pressure of between about 50 and about 300 p. s. i. is contemplated. The temperature within the alkylator 10 is maintained within the range of between about 400 and about 600° F., for example, about 450° F. If desired, 0.5 to about 2% of feed can comprise an alcohol, which may correspond to the alkylating olefin, to maintain the proper degree of hydration in the phosphoric acid catalyst, and to supply part of the olefins. Aluminum chloride hydrocarbon complex is useful in ethylene alkylation and when the complex is used, the alkylation is effected at a temperature of between about 50 and 250° F. under superatmospheric pressure.

The alkylation product is withdrawn from alkylator 10 by line 16 and introduced into absorber-separator 17. In absorber 17 the alkylate stream containing light gases which were introduced into

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10 with the olefins and/or aromatics is contacted with a recycle polyalkylaromatic hydrocarbon stream supplied by line 18. This fraction is higher boiling than is generally considered suitable or desirable in gasoline streams and may contain such aromatics as diethylbenzene, ethyltoluene, triethylbenzene, propyltoluene, etc. Extraneous polyalkylaromatics can be introduced by line 33. The separator-absorber 17 is maintained at a pressure within the approximate range of about atmospheric to about 500 pounds per square inch and at temperatures within the approximate range of 50 to 150° F. The unabsorbed diluent gases, substantially olefin- and benzene-free, pass overhead through line 20 while the enriched polyalkylbenzenes are withdrawn from absorber through line 21 and directed via line 22 to disproportionator 13.

The material removed by line 20 may comprise a cut boiling up to about 220° F. and can be subjected to a catalytic conversion wherein the diluent hydrocarbons are removed and a more concentrated benzene is recovered for recycle to the alkylation. Suitable catalysts are hydroforming and cracking catalyst. If desired the catalytic conversion can be the source of the dilute benzene stream, i. e., a hydroforming or a catalytic aromatizing of naphtha. Thus the inert diluent and residual benzene is recycled to the source which may suitably be hydroforming.

The polyalkylbenzene cut or a fraction thereof in line 21 is then contacted in the presence of an alkylation catalyst with concentrated benzene introduced into the disproportionation reactor 13, for example, by line 23 and recycled from fractionator 30 by lines 24, 25 and 26. Concentrated benzene sufficient for the disproportionation can be recovered from a portion of the benzene alkylation feed charged by line 11 by azeotropic distillation or by introducing into the absorber 17 by line 27. A portion of the recycle benzene can be bled into the absorber-separator 17 by lines 25 and 28 to remove diluents which might accumulate.

In the event that the alkylation is conducted with lower olefin ratios to aromatics including substantial proportions of benzene the product in line 21 comprises substantially greater amounts of monoalkylbenzene and the entire stream may be introduced into a separator (not shown) for the recovery of a monoalkylbenzene cut boiling up to about 350° F. and of a heavier polyalkylbenzene cut. The lighter fraction can be withdrawn for blending with a base stock since it will not contain substantial amounts of hydrocarbons boiling below about 220° F., or it can be introduced into the fractionator 30 for the recovery of monoalkylbenzene. Such an operation bypasses the disproportionator 13 with the result that optimum amounts of monoalkylbenzenes will result from the disproportionation of the predominantly polyalkylaromatic portion which is sent to 13.

The reaction in disproportionator 13 is essentially one of dealkylation of the polyalkylbenzene in the presence of excess benzene which in turn is alkylated primarily to monoalkylbenzene. The mol ratio of benzene to polyalkylbenzenes introduced into disproportionator 13 should be at least 1:1 and preferably greater than the number of mols of olefin attached as the alkyl groups to the polyalkylbenzenes. Higher temperatures such as those within the range of between about 500 and about 700° F., for example 650° F., are suitable with phosphoric acid alkylation catalyst and the

catalyst employed therein should be at least as active as that used in alkylator 10.

One mol of polyisopropylbenzene was disproportionated with two mols of benzene over solid phosphoric acid catalyst at 660° F. and 250 p. s. i. to yield 36 vol.% benzene, 36 vol.% monoalkylbenzene and 28 vol.% polyalkylbenzene. At 450° F. 42% benzene, 55 vol.% polyalkylbenzene and only 3 vol.% monoalkylbenzenes were recovered. This demonstrates that temperature is an important variable.

When the catalyst is aluminum chloride complex the disproportionation takes place in the presence of a molar excess of benzene at a temperature of between about 100 and 300° F., for example at about 200° F., and under pressures of between about 100 and 300 pounds per square inch. Two mols of benzene and one mol of diethylbenzene were maintained at 205–210° F. in the presence of 7% aluminum chloride and HCl was passed through the stirred mixture. The cooled products were separated into an upper layer representing 85% of the hydrocarbon and a lower catalyst layer. The hydrocarbon layer contained 42% benzene, 43% ethylbenzene and 15% diethylbenzene and heavier. It is contemplated that hydrogen fluoride can be used to effect a similar reaction at temperatures above alkylation temperatures and under sufficient pressure to maintain the liquid phase.

The disproportionation product is withdrawn by line 29 from disproportionator 13 and introduced into product fractionator 30. The products can be fractionated to yield a benzene fraction, a monoalkylbenzene fraction, an intermediate alkylbenzene fraction predominating in light polyalkylbenzenes and a heavy polyalkylbenzene fraction. The desired monoalkylbenzene cut is withdrawn from fractionator 30 by line 31. A benzene overhead cut ordinarily is recycled by lines 24 and 25 either to the disproportionation reactor 13 directly by line 26 or to the separator-absorber 17 by lines 25 and 28. The heavy polyalkylbenzene fraction is returned to absorber 17 via line 18, while the intermediate alkylbenzene fraction comprising light polyalkylbenzenes is withdrawn through line 14, and is preferably directed to alkylator 10 via lines 11 and 12. A light alkylbenzene fraction can be withdrawn by line 32 for use, for example, as a solvent. The lighter polyalkylbenzenes added to the alkylator 10 are converted in alkylator 10 to higher boiling polyalkylbenzenes by olefins introduced at 15 as hereinbefore described. In this manner of operation only the light polyalkylbenzenes are subjected to further alkylation and substantially only polyalkylbenzenes are introduced into the disproportionation zone with benzene. Only the heaviest polyalkylbenzenes are employed as an absorbing medium, and loss of light products by the sweeping effect of the entering gases is substantially eliminated. It is possible to use in the disproportionation a benzene cut having 60 to 100% benzene and to recycle the unreacted benzene fraction until the concentration becomes uneconomic at which time it can be recycled to the alkylation zone 10 to be converted to mono- and polyalkylbenzenes which are subsequently disproportionated in the disproportionator 13. If desired, the entire benzene fraction for disproportionation can be supplied via the separator-absorber system.

It is contemplated that the alkylator 10 and the disproportionator 13 can be used alternately for alkylation and disproportionation by provid-

ing the necessary conduits and valves. Thus one can be used at a lower temperature to effect alkylation and then used at the higher temperature for disproportionation or the sequence can be reversed.

It should be understood that the alkylation and disproportionation steps may comprise two or more stages and that additional apparatus can be supplied when necessary, for example, when using aluminum chloride hydrocarbon complex or hydrogen fluoride as the catalyst. In that event the alkylation zone 10 and disproportionator 13 will include an alkylator provided with means for withdrawal of catalyst and reactants into a settling chamber from which the catalyst is recycled to the alkylator, the hydrocarbon fraction separated, and scrubbed with dilute caustic before introduction into the absorber 17 or product fractionator 30. Spent catalyst may be withdrawn from either the alkylator or disproportionator. Likewise catalyst used in either zone may be transferred to the other. The absorber-separator system 17 can be in stages, either series or parallel. Monoalkylbenzene trapout can be provided on 17.

From the foregoing it will be apparent that I have attained the objects of my invention and have provided a new process for the production of optimum quantities of monoalkylbenzenes by a combination of integrated steps wherein aromatics are alkylated with olefins to produce higher boiling aromatics, alkylaromatics heavier than the desired monoalkylbenzene are cut into light and heavy fractions, the light is further alkylated in the first step with an olefin stream and goes to an absorber-separator where it is scrubbed with the heavy polyalkylaromatic. The combined streams of alkylaromatics go to a disproportionator for the production of additional monoalkylbenzene. Thus an optimum fraction is further alkylated to effect optimum olefin and benzene cleanup and optimum feed is provided for the disproportionation.

Although I have described my process with special reference to embodiments thereof it should be understood that this is by way of illustration only and not by limitation and that I intend to be limited only to the extent set forth in the appended claims. Moreover various details such as pumps, heat exchangers, automatic control devices and the like have been omitted from the drawing and the description thereof for the sake of simplicity and clarity.

I claim:

1. A process for the production of monoalkylbenzenes which comprises supplying an olefin-containing stream and alkylated mononuclear aromatics to an alkylation zone, further alkylating said aromatics with said olefins in the presence of an alkylation catalyst within said zone, withdrawing the alkylation products from said zone, introducing the alkylation products and unreacted hydrocarbons into a gas separation zone, introducing into said separation zone a relatively cool polyalkylated aromatic liquid fraction hereinafter derived, withdrawing gases overhead from said separation zone recovering a combined liquid stream from said separation zone comprised essentially of polyalkylated aromatics, commingling benzene with said polyalkylated mononuclear aromatics contacting said polyalkylated aromatics and a molar excess of benzene with another quantity of said alkylation catalyst, maintaining the temperature within said contacting zone substantially above that maintained in the

alkylation zone whereby substantial proportions of said polyalkylaromatic and of said benzene are converted to monoalkylaromatic hydrocarbons, withdrawing the products from said second contacting step, recovering at least one monoalkylbenzene fraction, an intermediate alkylaromatic fraction and a heavy polyalkylaromatic fraction, and supplying said intermediate alkylaromatic fraction to the first-mentioned alkylation step, at least a portion of said heavy polyalkylaromatic fraction being the liquid fraction introduced into said separation step.

2. A process for the production of an aviation gasoline constituent which comprises supplying an olefin-containing stream and mononuclear aromatic-containing stream to an alkylation zone, alkylating said aromatics with said olefins within said zone in the presence of a phosphoric acid alkylation catalyst, withdrawing the alkylation products from said zone, introducing the alkylation products and unreacted hydrocarbons into a gas separation zone, introducing into said separation zone a polyalkylated mononuclear aromatic liquid fraction hereinafter derived, withdrawing gases overhead from said separation zone, recovering a combined liquid stream from said separation zone comprised essentially of polyalkylated aromatics, commingling benzene with said polyalkylated mononuclear aromatics reacting said polyalkylated aromatics and a molar excess of benzene in the presence of another quantity of phosphoric acid alkylation catalyst, maintaining the temperature during said reaction substantially above that maintained in the alkylation zone whereby substantial proportions of said polyalkylaromatic and of said benzene are converted to monoalkylaromatic hydrocarbons, withdrawing the products from said second reaction step, recovering from the reaction product at least one fraction suitable as an aviation gasoline constituent, an intermediate alkylaromatic fraction and a heavy polyalkylaromatic fraction, and supplying said intermediate alkylaromatic fraction to the first-mentioned alkylation step and at least a portion of said heavy fraction to the separation zone.

3. A process for the production of alkylbenzenes in the aviation gasoline boiling range which comprises supplying an olefin and a stream of hydrocarbons including mononuclear aromatics to an alkylation zone in a mol ratio of olefin to aromatic of at least 1:1, reacting the said olefin and aromatics in the presence of an alkylation catalyst within said zone under alkylation conditions of temperature and pressure, withdrawing the reaction products from said zone, introducing the reaction products at a low point in a separation zone, introducing a polyalkylated aromatic fraction hereinafter derived into said separation zone at a relatively high point therein, withdrawing the gases overhead from said separation zone, withdrawing a liquid stream of polyalkylated aromatics from said separation zone, commingling benzene with said polyalkylated mononuclear aromatics, contacting in the presence of another quantity of said alkylation catalyst said reaction products together with sufficient added benzene to give a ratio of total mononuclear aromatic hydrocarbons to alkyl groups of greater than 1:1, maintaining the temperature within said second contacting zone substantially above that maintained in the alkylation zone whereby substantial proportions of said polyalkylaromatic and of said benzene are converted

to monoalkylbenzene, withdrawing the conversion products from said second contacting zone, separating said conversion products into a benzene fraction, a monoalkylbenzene fraction, an intermediate alkylaromatic fraction and a heavy polyalkylaromatic fraction, introducing said heavy alkylaromatic fraction into the aforementioned separation zone, and supplying at least a portion of the intermediate alkylaromatic fraction to the first-mentioned alkylation.

4. A process for the production of monoalkylaromatic hydrocarbons in the aviation gasoline boiling range which comprises subjecting an olefin stream diluted with light paraffins and a stream of hydrocarbons including mononuclear alkylaromatics to alkylation in the presence of an alkylation catalyst to produce predominantly polyalkylaromatics, withdrawing the reaction products and unreacted hydrocarbons from said alkylation, introducing the reaction products and unreacted hydrocarbons into a gas separation zone, introducing a polyalkylated aromatic liquid fraction hereinafter derived into said separation zone at a relatively high point therein, withdrawing diluent hydrocarbons overhead from said separation zone, withdrawing from said separation zone a liquid stream of polyalkylated aromatics, introducing benzene and said polyalkylated aromatics into a second contacting zone, contacting said polyalkylaromatics together with said benzene in the presence of another quantity of said alkylation catalyst in a mol ratio of benzene nucleus to alkyl group of greater than 1:1 in said second contacting step whereby substantial proportions of said polyalkylaromatic and of said benzene are disproportionated to produce monoalkylaromatic hydrocarbons, withdrawing the products from said second contacting step, recovering from said products a benzene fraction, a monoalkylbenzene fraction, an intermediate alkylaromatic fraction and a heavy polyalkylaromatic fraction, introducing said heavy alkylaromatic fraction into the aforementioned gas separation zone, and supplying at least a portion of the intermediate alkylaromatic fraction to the first-mentioned alkylation step.

5. A process for the production of monoalkylaromatic hydrocarbons in the aviation gasoline boiling range which comprises subjecting olefinic and aromatic hydrocarbon fractions in a mol ratio of olefin to aromatic of at least 1:1 to alkylation in the presence of an alkylation catalyst, introducing the reaction products and a gaseous benzene-containing stream at a low point into a gas separation zone, introducing into said separation zone at a relatively high point therein polyalkylated aromatic fraction hereinafter derived, withdrawing gases overhead from said separation zone, withdrawing a combined liquid stream of benzene and polyalkylated aromatics from said separation zone, reacting said stream in the presence of another quantity of said alkylation catalyst in a second contacting zone wherein the mol ratio of benzene to alkyl is greater than 1:1, maintaining the temperature during said second reaction substantially above that maintained in the alkylation step whereby substantial proportions of said polyalkylaromatic and of said benzene are converted to monoalkylaromatic hydrocarbons, withdrawing the conversion products from said second contacting zone, separating said conversion products into a benzene fraction, a monoalkylbenzene fraction, an intermediate alkylaromatic fraction and a heavy polyalkylaromatic fraction, introducing said heavy alkylaromatic fraction into the aforementioned gas separation zone, and supplying at least a portion of the intermediate alkylaromatic fraction to the first-mentioned alkylation step.

matic fraction into the aforementioned separation zone, supplying at least a portion of the intermediate alkylaromatic fraction to the first-mentioned alkylation step, and recycling said benzene fraction to said last-mentioned reaction step.

6. A process for the production of mononuclear alkylaromatic hydrocarbons boiling within the aviation gasoline range which comprises supplying an olefin and a stream of hydrocarbons including mononuclear alkylaromatics to an alkylation zone, reacting the said olefin and aromatics in the presence of an alkylation catalyst within said zone under alkylation conditions to produce alkylated mononuclear aromatics of higher boiling point, introducing the reaction products and unreacted hydrocarbons at a low point into a gas separation zone, introducing into said separation zone at a relatively high point therein a second polyalkylated aromatic fraction hereinafter derived, withdrawing gases overhead from said separation zone, withdrawing a combined liquid stream of polyalkylated aromatics from said separation zone, introducing benzene and said polyalkylaromatics into a second contacting zone, contacting said reaction products together with additional amounts of a benzene fraction with another quantity of said alkylation catalyst in said second contacting zone, maintaining the temperature within said second contacting zone substantially above that maintained in the alkylation zone whereby substantial proportions of said polyalkylaromatic and of said added aromatic are converted to monoalkylaromatic hydrocarbons, withdrawing the conversion products from said second contacting zone, recovering from said conversion products a benzene fraction, a monoalkylbenzene fraction, an intermediate alkylaromatic fraction and a heavy polyalkylaromatic fraction, supplying said heavy polyalkylaromatic fraction to the aforementioned separation zone, subjecting at least a portion of the intermediate alkylaromatic fraction to the first-mentioned alkylation, and recycling the benzene fraction to said second contacting step.

7. A process for the production of monoalkylbenzenes which comprises supplying olefins and mononuclear aromatics to an alkylation zone, alkylating said aromatics with said olefins in the presence of an alkylation catalyst within said zone, withdrawing the alkylation products from said zone together with unreacted hydrocarbons, introducing the alkylation products and unreacted hydrocarbons into a gas separation zone, introducing into said separation zone a relatively cool polyalkylated mononuclear aromatic liquid fraction hereinafter derived, withdrawing gases overhead from said separation zone, recovering a combined liquid stream from said separation zone comprising essentially polyalkylated aromatics introducing benzene and said polyalkylaromatics into a conversion zone, contacting said polyalkylated aromatics and a molal excess of said benzene in the presence of another quantity of said alkylation catalyst at a higher temperature than employed in the alkylation whereby substantial proportions of said polyalkylaromatic and of said benzene are converted to monoalkylbenzene, recovering a monoalkylbenzene fraction, an intermediate alkylaromatic fraction, and a heavy polyalkylaromatic fraction from the conversion products, and supplying at least a portion of said heavy polyalkylaromatic fraction to said gas separation step.

8. A process for the production of monoalkylaromatic hydrocarbons in the aviation gasoline boiling range which comprises the steps of subjecting olefinic and mononuclear aromatic hydrocarbon fractions to alkylation in the presence of an alkylation catalyst, introducing the alkylation products and a gaseous benzene-containing stream at a low point into a gas separation zone, introducing into said separation zone at a relatively high point therein a polyalkylated mononuclear aromatic fraction hereinafter derived, withdrawing gases overhead from said separation zone, withdrawing a combined stream of benzene and liquid polyalkylaromatics from said separation zone, reacting said stream in the presence of another quantity of said alkylation catalyst in a second contacting zone, maintaining the temperature during said second reaction substantially above that maintained in the alkylation step whereby substantial proportions of said polyalkylaromatic and of said benzene are converted to monoalkylaromatic hydrocarbons, withdrawing the conversion products from said second contacting zone, separating said conversion products to include at least a monoalkylbenzene fraction and a heavy polyalkylaromatic fraction, and supplying at least a portion of said heavy polyalkylaromatic fraction to said gas separation zone.

9. A process for the production of alkylbenzenes which comprises supplying mononuclear aromatics and olefins to an alkylation zone, alkylating said aromatics with at least a portion of said olefins in the presence of an alkylation catalyst within said zone, withdrawing the total alkylation product stream from said zone including liquid alkylation products and unreacted hydrocarbons, introducing liquid alkylation products and unreacted hydrocarbons at a low point into an absorber zone, introducing a relatively cool polyalkylated aromatic liquid fraction at a high point in said absorber zone, withdrawing overhead from said absorber zone a gaseous fraction, recovering a combined liquid stream from said absorber step comprising essentially polyalkylated mononuclear aromatics and absorbed hydrocarbons, introducing benzene and said polyalkylated mononuclear aromatics into a conversion zone, contacting said polyalkylated aromatics with another quantity of said alkylation catalyst in the presence of a molal excess of said benzene within said conversion zone whereby substantial proportions of said polyalkylaromatic and of said benzene are converted to monoalkylaromatic hydrocarbons, withdrawing the products from said second catalytic contacting step, recovering a monoalkylbenzene fraction, an intermediate liquid alkylaromatic fraction, and a heavy polyalkylaromatic fraction, supplying at least a portion of said intermediate alkylaromatic fraction to the first-mentioned alkylation step, and supplying at least a portion of said heavy polyalkylaromatic fraction to said absorption step.

10. A process for the production of monoalkylaromatic hydrocarbons comprising the steps of alkylating a mononuclear aromatic hydrocarbon with concomitant dealkylation of a polyalkylaromatic hydrocarbon in the presence of an alkylation catalyst under alkylation conditions adapted to yield both mono and polyalkylaromatic hydrocarbons, separating from the reaction product a monoalkylaromatic hydrocarbon fraction and relatively high and relatively low boiling fractions of polyalkylated mononuclear aromatic hydrocarbons, alkylating at least a portion of the relatively low boiling polyalkylaromatic hydro-

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carbons with olefins from a dilute stream to produce high boiling polyalkylated mononuclear aromatics, contacting a gas stream containing reactant hydrocarbons with at least a portion of the relatively high boiling polyalkylbenzene whereby reactant hydrocarbons are adsorbed therein, and supplying said high boiling polyalkylated aromatic hydrocarbon fraction to said first alkylation step.

11. A process for the production of predominately monoalkylbenzene which comprises reacting an olefin-containing gas with a hydrocarbon mixture consisting essentially of benzene and of relatively low boiling polyalkylbenzenes produced in the system, said reaction being conducted in the presence of an alkylation catalyst under conditions to yield predominately polyalkylbenzenes, absorbing benzene in a fraction of relatively high boiling polyalkylbenzenes produced in the system, reacting the mixture of polyalkylbenzenes and benzene with a second quantity of similar alkylation catalyst at a higher temperature than employed in the first alkylation, recovery from the second alkylation an alkylate containing substantial amounts of monoalkylbenzene, together with a smaller proportion of polyalkylbenzene than in the alkylate from the first alkylation zone,

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separating the polyalkylbenzenes into a relatively light polyalkylbenzene and a relatively heavy polyalkylbenzene, and supplying said fractions to the said first reaction step and to said absorption step, respectively.

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