

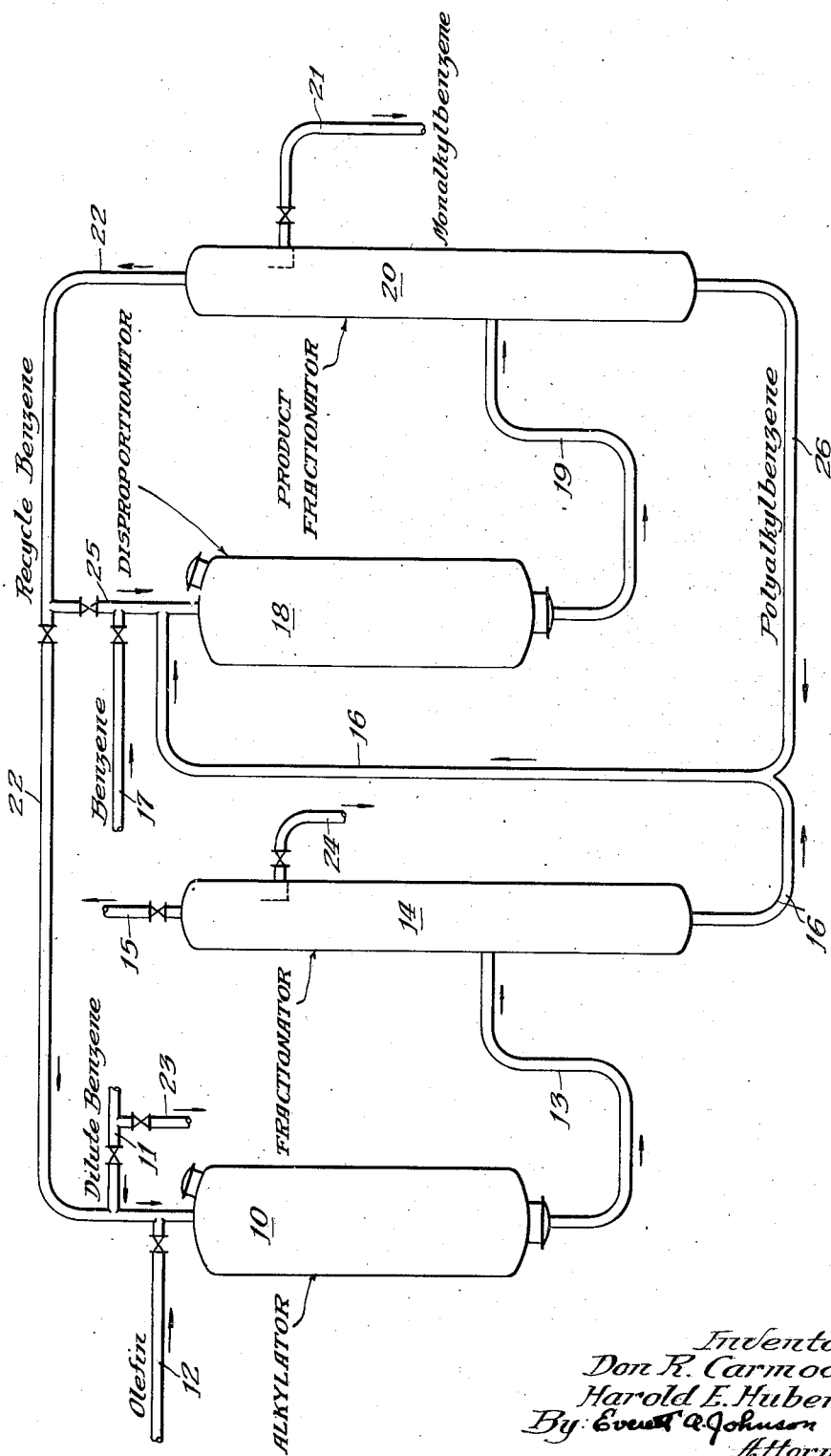
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D. R. CARMODY ET AL

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PRODUCTION OF ALKYL BENZENE

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Inventors:
Don R. Carmody,
Harold E. Huber, Jr.
By: Ernest A. Johnson
Attorney:

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PRODUCTION OF ALKYL BENZENE

Don R. Carmody, Hammond, Ind., and Harold E. Huber, Chicago, Ill., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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This invention relates to the production of alkyl aromatic hydrocarbons and relates more particularly to the production of monoalkyl benzene by the alkylation of benzene from a dilute benzene stream with propylene.

Monoalkyl benzenes and particularly the lower boiling monoalkyl benzenes such as butylbenzene and isopropylbenzene (cumene) have been found to be valuable constituents of aviation fuels because of their very high octane number, particularly under "supercharged" conditions. The amount of monoalkyl benzenes 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 and the like, the ultimate yield of low boiling alkyl benzene aromatics is comparatively low. Higher boiling aromatics, such as xylene, are obtained in much higher yield by thermal cracking, catalytic cracking, or hydroforming. However, the paraffins contained in such fractions have relatively low octane numbers and should be excluded from aviation gasoline in order to reduce the cumene requirements to a very minimum.

It has been known for some time that these desirable alkyl benzenes can be synthesized by the alkylation of benzene with olefins in the presence of suitable catalysts. The above processes give rise to some benzene but the actual volume is low and the benzene is present only in low concentrations. Concentration of all of the dilute benzene by various means such as by azeotropic distillation, fractional condensation, solvent extraction, adsorption, and the like has not been practicable. Consequently dilute benzene has not been an economical source of benzene for alkylation which heretofore has required concentrated benzene derived from coal tars, for example. 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 the unreacted benzene to the alkylation is not feasible because of the inert diluent.

It is an object of this invention to provide an improved process for the economical alkylation of an aromatic from an aromatic-containing dilute stream with olefinic hydrocarbons. Another object of our invention is to provide an improved process for the production of monoalkyl benzenes from dilute benzene-containing streams wherein the necessity for concentrating the benzene is reduced to a minimum. A still further object of our invention is to provide an integrated process wherein hydrocarbons valuable for aviation fuels are prepared from a dilute benzene stream by a combination of steps. Further objects and advantages will become apparent as the description of our invention proceeds.

Briefly stated our invention contemplates a unitary process including the alkylation of a dilute benzene hydrocarbon stream with an excess of olefins by contacting in the presence of an alkylation catalyst at temperatures within the range of between about 400 and about 600° F. When propylene is the olefin the benzene is alkylated from the stream to produce cumene and polyisopropylbenzene. Another step in our unitary process is subjecting the alkylate comprising polyalkylbenzenes to disproportionation in the presence of added benzene and the alkylation catalyst, such as solid phosphoric acid, at a higher temperature above about 450° F. within the range of between about 500 and 700° F. to produce additional monoalkyl benzenes by a dealkylation-alkylation. A recycle benzene fraction and a polyalkyl benzene fraction can be returned to the disproportionation to form additional monoalkyl benzenes. When the benzene content of the recycle benzene from the disproportionation step becomes diluted it may be recycled to the dilute benzene alkylation step to produce additional polyalkyl benzenes.

When operating with dilute benzene it is necessary to employ propylene-benzene mol ratios higher than one in order to remove most of the benzene. 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 cumene and 25% is polyisopropylbenzene. By increasing the propylene-benzene mol ratio, the benzene cleanup can be increased to 75% under which conditions the alkylate contains about equal amounts of cumene and polyisopropylbenzene. Thus the use of a molar excess of olefins to effect high benzene cleanup from dilute streams produces higher boiling polyalkylbenzenes unsuitable for use as motor or aviation fuel. The latter product can be disproportionated with concentrated benzene at somewhat higher temperatures, i. e. about 500° F. as compared with 450° F. for alkylation, both for example in the presence of phosphoric acid catalyst.

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

Referring to the drawing a dilute benzene stream, 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 line 11. The dilute benzene stream may contain between about 10% and about 75% benzene. An olefin such as propylene is introduced by line 12 in an amount such as to maintain a mol ratio of propylene to benzene within the alkylator 10 of between about one and

about five or higher, for example above about 2.5. 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 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 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 the catalyst is maintained in a highly dispersed phase or in a dense, turbulent, fluent phase may be used. The temperature within the alkylator 10 is maintained within the range of between about 400 and about 600° F., for example 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. The alkylation product is withdrawn from alkylator 10 by line 13 and introduced into fractionator 14 wherein the reaction product is separated into an overhead cut having a maximum end point of about 220° F. which is withdrawn by line 15. A monoalkylbenzene cut boiling up to about 350° is withdrawn through line 24 and a higher boiling polyalkylbenzene cut is removed as bottoms by line 16.

The overhead cut boiling up to about 220° F. can be subjected to a catalytic conversion wherein the inert diluent is removed and the more concentrated benzene is recycled to the alkylation. Suitable catalysts are hydroforming and solid cracking catalyst. If desired the catalytic conversion can comprise the source of the dilute benzene stream, i. e. a hydroforming or catalytic aromatizing of naphtha. Thus the inert diluent and residual benzene is recycled to the source which may suitably be hydroforming. Merely recycling the diluent and unreacted benzene to the alkylation would only further dilute the stream.

The predominantly polyalkylbenzene cut or a fraction thereof in line 16 is then contacted in the presence of an alkylation catalyst, such as a supported phosphoric acid catalyst, with concentrated benzene introduced into the disproportionation reactor 18, for example, by line 17 and recycled by lines 22 and 25. Concentrated benzene sufficient for the disproportionation can be recovered from a portion of the dilute benzene alkylation feed withdrawn for example by line 23. Any desired means of concentration can be used as, for example, an azeotropic distillation. When necessary a portion of the recycle benzene can be bled into the concentrator to remove diluents which might accumulate.

The temperature within the disproportionation zone is maintained within the range of between about 500° F. and about 700° F., for example, at about 650° F. The disproportionation product is withdrawn by line 19 and introduced into product fractionator 20. The desired monoalkylbenzene cut is withdrawn from fractionator 20 by line 21. A benzene overhead cut ordinarily is recycled by line 22 either to the disproportionation reactor 18 or to alkylator 10. An unreacted polyalkylbenzene fraction is withdrawn by line 26 and recycled to the disproportionator 18 by line 16. It is possible to use in the disproportiona-

tion a benzene cut having 60 to 100% benzene and to recycle the unreacted benzene fraction until the concentration becomes uneconomical 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 18 or withdrawn, concentrated, and returned via line 17.

It is contemplated that the alkylator 10 and the disproportionator 18 can be used alternately for alkylation and disproportionation by providing the necessary conduits and valves. Thus one can be used at a lower temperature with fresh catalyst to effect alkylation and then used at the higher temperature for disproportionation. Two or more reactors can be used in stages, series or parallel.

The examples set forth in the following Table I illustrate the importance of the use of the proper mol ratio of the reactants and low feed rates in the alkylation. In each of the runs the catalyst was phosphoric acid on kieselguhr.

Table I

	Example			
	1	2	3	4
Temperature.....°F	450	460	460	455
Pressure.....p. s. i.	250	255	250	250
Mol ratio C ₆ H ₆ /C ₃ H ₆	28	1.0	2.5	2.5
Rate.....gal./hr./lb.	0.22	0.21	0.24	0.05
Product analysis, volume per cent:				
Benzene cut.....	39	19	12	5
Isopropylbenzene cut.....	12	30	26	31
Polyisopropylbenzene cut.....	2	12	21	25
35 Benzene reacted.....weight per cent.	19	49	55	80
Isopropylbenzene, per cent of total alkylate.....	86	76	55	55

From the above Table I it is apparent that by using a mol ratio of propylene to benzene less than one the benzene cleanup is insufficient to establish an economical process since it is not feasible to recycle the unreacted benzene plus the inert diluent. When the propylene to benzene ratios are low, the per cent monoalkylate in the total alkylate produced is highest. However, the volume of isopropylbenzene per unit volume of product is greater when ratios greater than one are used. The importance of low feed rates is shown in Example 4 wherein 80% of the benzene was reacted without unfavorably affecting the per cent isopropylbenzene produced per unit volume of product.

The polyalkyl benzene produced in the alkylation is converted to the monoalkylbenzenes by disproportionation over solid phosphoric acid at a temperature in excess of 450° F. The data set forth in the following Table II indicates the importance of temperature in the disproportionation.

Table II

	Example				
	5	6	7	8	9
Temperature.....°F	440	555	450	550	660
Pressure.....p. s. i.	230	250	250	50	250
Rate.....gal./hr./lb. cat.	0.12	0.08	0.05	0.09	0.09
Feed, weight per cent:					
t-Butyl alcohol.....	72.2	72.2	1.4	1.4	1.4
Benzene.....	27.8	27.8	48.6	48.6	48.6
Polyisopropylbenzene.....			50.0	50.0	50.0
70 Mol ratio C ₆ H ₆ /polyisopropylbenzene.....	4.0	4.0	2.09	2.09	2.09
Product analysis, volume per cent:					
Benzene.....	71	85	42	45	36
Monoalkylbenzene.....	5	23	3	18	36
Polyalkylbenzene.....	24	12	55	37	28

From the above it is apparent that the reaction at 450° F. and below is negligible, but even at these low temperatures the reaction is greater with lower feed rates. At 550° F. the production of monoalkylates is appreciable. At 660° F. the reaction proceeds smoothly. The effect of pressure is illustrated in Examples 6 and 8 from which it is apparent that at the lower pressures the yield of monoalkylate is perhaps slightly reduced, but not to any appreciable extent.

A disproportionation similar to that illustrated in Table II does not result when the substituent alkyl group has but one carbon atom to the molecule. Xylenes from which all toluene was carefully removed was diluted with an equal volume of benzene and passed over phosphoric acid catalyst under pressure of 250 P. S. I. for 3.3 hours at a rate of 0.10 gal./hr./lb. at both 550° F. and 650° F. Careful fractionation of the liquid products gave no trace of toluene in either case.

By our process large quantities of a very desirable product are produced from a material heretofore considered wholly unsatisfactory for the purpose. The necessity of concentrating large quantities of dilute benzene is avoided and the only benzene which need be concentrated is that used in the disproportionation of the polyalkylbenzenes. By controlling the mol ratio of the olefin to benzene in the alkylation step, an optimum amount of mono- and polyalkylbenzenes is produced. The disproportionation of these polyalkylbenzenes with concentrated benzene is effected at low feed rates and in the presence of a catalyst of the same composition as the alkylation catalyst, but at a higher temperature. In one embodiment of our invention, the residual benzene and inert diluent recovered from the alkylation step is recycled to the catalytic conversion step which provides the dilute benzene stream.

From the foregoing it will be apparent that we have attained the objects of our invention and have provided a new process for the production of monoalkylbenzenes from dilute benzene by a combination of integrated steps.

Although we have described our process with special reference to one embodiment thereof it should be understood that this is by way of illustration only and not by limitation and that we 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.

We claim:

1. A process for the production of isopropylbenzene which comprises alkylating a dilute benzene hydrocarbon mixture with propylene in the presence of a phosphoric acid alkylation catalyst under alkylation conditions at a temperature below about 450° F., the mol ratio of propylene to benzene being greater than one, recovering a fraction of the alkylation product having an initial point above about 350° F. and contacting the said fraction with added benzene at a temperature in excess of about 450° F. in the presence of a phosphoric acid alkylation catalyst whereby at least a portion of the added benzene is alkylated.

2. A process for the production of isopropylbenzene which comprises contacting dilute benzene and propylene under alkylating conditions in the presence of a phosphoric acid catalyst, the

ratio of propylene to benzene being about three to one, thereby converting a substantial fraction of the benzene to isopropylbenzene and polyisopropylbenzene, disproportionating the polyisopropylbenzene to isopropylbenzene by contacting with added benzene in the presence of a phosphoric acid catalyst at a temperature substantially above that maintained in the alkylation, and at a feed rate of about 0.01 to 1.0 gal./hr./lb. of catalyst.

3. A process for the production of isopropylbenzene which comprises contacting propylene and a dilute benzene hydrocarbon mixture in the presence of an alkylation catalyst under alkylation conditions at a temperature not in excess of about 450° F., maintaining the mol ratio of propylene to benzene greater than one, subjecting a fraction of the alkylation product comprising polyisopropylbenzene to a disproportionation, said disproportionation being effected by contacting the alkylate with added benzene at a temperature in excess of 450° F. in the presence of a catalyst of the composition employed in the said alkylation, thereby producing additional quantities of isopropylbenzene.

4. The process for the production of monoalkyl aromatic hydrocarbons which comprises subjecting a mixture of concentrated olefin and dilute benzene to alkylation in the presence of phosphoric acid thereby producing an alkylate comprising a mixture of mono- and polyalkylbenzenes, subjecting the polyalkylate to disproportionation in the presence of phosphoric acid and added benzene under conditions of temperature and pressure more severe than employed in the alkylation, recovering a recycle benzene fraction, a monoalkylbenzene fraction, and a polyalkylbenzene fraction from said disproportionation, recycling the polyalkylbenzene fraction to the said disproportionation and flowing said dilute recycle benzene fraction to the said alkylation.

5. The process for the production of monoalkyl aromatic hydrocarbons which comprises subjecting a mixture of concentrated olefin and dilute benzene to alkylation in the presence of phosphoric acid thereby producing an alkylate comprising a mixture of mono- and polyalkylbenzenes, subjecting the polyalkylate to disproportionation in the presence of phosphoric acid and added benzene at a temperature above that employed in the alkylation step, recovering a recycle benzene fraction, a monoalkylbenzene fraction and a polyalkylbenzene fraction from said disproportionation, recycling the polyalkylbenzene fraction to the said disproportionation, recycling the benzene to the said disproportionation step so long as the concentration of the benzene therein is in excess of 60%, and flowing the recycle benzene having a concentration below about 60% to the said alkylation step wherein the benzene is alkylated to mono- and polyalkylbenzenes.

6. The production of a super aviation fuel component by a combination of processes including alkylating a dilute benzene stream with propylene at a temperature at about 450° F. in the presence of a supported phosphoric acid catalyst, contacting the polyalkylate with a second quantity of a supported phosphoric acid catalyst at a temperature above about 450° F. and recovering from said contacting step a monoalkylate fraction which predominates in isopropylbenzene.

7. A process for the production of isopropylbenzene which comprises contacting propylene and a dilute benzene hydrocarbon mixture in the presence of a solid alkylation catalyst under

alkylation conditions at a temperature not in excess of about 450° F., maintaining the mol ratio of propylene to benzene within the alkylation zone at a value greater than one, recovering a light fraction from the alkylation having an end point of about 220° F. and an isopropylbenzene cut, and converting the residual alkylation product including polyisopropylbenzene into isopropylbenzene by contacting the residual alkylate with added benzene at a temperature in excess of about 450° F. in the presence of a solid alkylation catalyst of the composition employed in said alkylation.

8. A process for the production of monoalkylaromatic hydrocarbons in the gasoline boiling range which comprises supplying an olefin and a stream of hydrocarbons including 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 phosphoric acid alkylation catalyst within said zone under alkylation temperature, withdrawing reaction products including polyalkylaromatics from said zone, passing said reaction products together with additional amounts of aromatics over a phosphoric acid catalyst in a mol ratio of aromatic to polyalkylaromatic of greater than 1:1 in a second contacting zone, maintaining the temperature within said second contacting zone substantially above that maintained in the alkylation zone, whereby substantial proportions of said added aromatic is converted to alkyl aromatic and substantial proportions of said polyalkylaromatic is converted to monoalkylaromatic, withdrawing and separating the conversion products, and recycling unalkylated aromatics to said second contacting step.

9. A process for the production of monoalkylbenzenes which comprises supplying a mixture of hydrocarbons including olefins and benzenes to a first contacting zone, maintaining a mol ratio of olefin to benzene greater than one in the feed to said zone, contacting said hydrocarbons with a phosphoric acid alkylation catalyst within said zone, withdrawing reaction products from said zone and recovering the polyalkylbenzene fraction having an initial boiling point of at least

350° F., supplying said polyalkylbenzene along with added benzene to a second contacting zone, maintaining a mol ratio of benzene to alkyl benzene of at least 4:1 in the feed to said contacting zone, contacting said polyalkylbenzene and added benzene with a phosphoric acid alkylation catalyst at a temperature in excess of 500° F. within said second contacting zone whereby a substantial proportion of the polyalkylbenzene is converted to monoalkylbenzene and a proportion of the benzene is alkylated to monoalkylbenzene, separating the reaction products to recover at least one fraction including benzene and recycling the benzene to the said second contacting step.

10. A process for the production of isopropylbenzene which comprises supplying propylene and benzene diluted with other hydrocarbons to a first contacting zone, the ratio of propylene to benzene being at least 1:1, reacting the propylene and benzene in said contacting zone in the presence of a phosphoric acid alkylation catalyst to produce a mixture of isopropylbenzene and polyisopropylbenzenes, and contacting the polyisopropylbenzene and added benzene in a second contacting zone in the presence of a phosphoric acid alkylation catalyst at a temperature substantially above that maintained in the first contacting zone, the mol ratio of benzene to polyisopropylbenzene feed to the second contacting zone being substantially greater than 1:1.

11. The process of making cumene which comprises the steps of alkylating dilute benzene and a molal excess of propylene in the presence of a solid alkylation catalyst at a temperature between about 400 and 600° F., and disproportionating diisopropylbenzene produced by said alkylation step, disproportionating being effected at a temperature higher than the temperature of the alkylation step and within the range of between about 500 and 700° F. in the presence of a disproportionation catalyst comprising a solid alkylation catalyst of the composition employed in the reaction which produced the diisopropylbenzene.

DON R. CARMODY.
HAROLD E. HUBER.