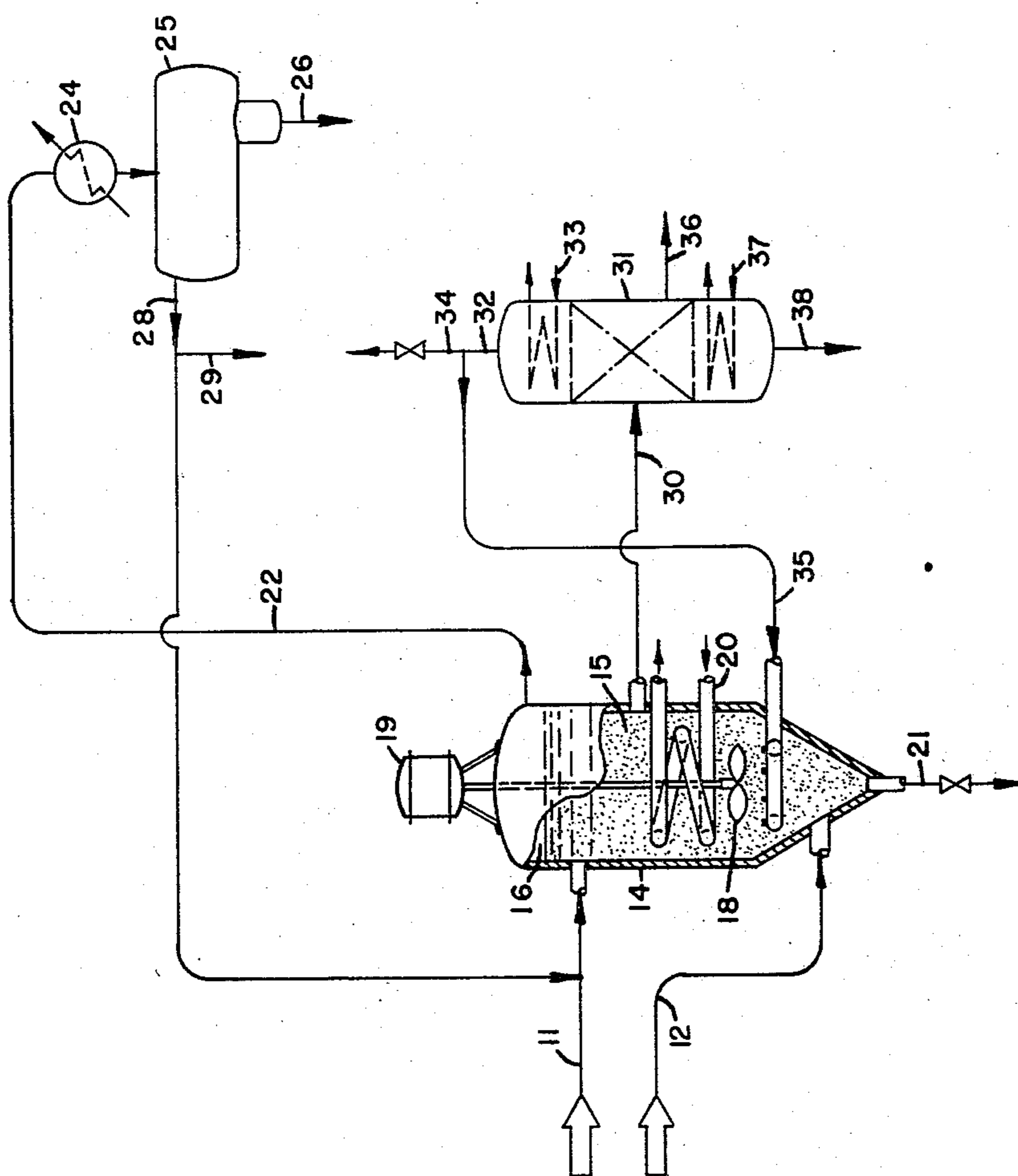


Sept. 2, 1958

L. C. FETTERLY ET AL
PREPARATION OF DIARYL METHANES

2,850,545

Filed Dec. 27, 1955



INVENTORS
LLOYD C. FETTERLY
KENNETH F. KOETITZ
DONALD W. PENHALE
BY *James J. O'Connor*
THEIR ATTORNEY

2,850,545

PREPARATION OF DIARYL METHANES

Lloyd C. Fetterly, El Cerrito, Kenneth F. Koetitz, Concord, and Donald W. Penhale, Berkeley, Calif., assignors to Shell Development Company, New York, N. Y., a corporation of Delaware

Application December 27, 1955, Serial No. 555,583

12 Claims. (Cl. 260—668)

This invention relates to a process for the production of diarylmethanes, and more specifically to a process for the production of diarylmethanes by condensation of aromatic hydrocarbons with formaldehyde in the presence of porous, solid, acidic catalysts.

It is a principal object of the present invention to provide an improved process for the production of condensation products of aromatic hydrocarbons and formaldehyde containing essentially only diarylmethanes and no more than a low concentration of triaryldimethanes (arylmethyl-diarylmethanes). It is a further object to provide an improved process for converting aromatic hydrocarbons and formaldehyde into diarylmethanes in high yield with high selectivity. A further object of the invention is to provide a commercially suitable process for the production of diarylmethanes. It is a specific object of the present invention to provide an improved method for preparing the bis-diarylmethane compounds in which the aryl groups are tolyl, xylyl, and trimethylphenyl, respectively. Other objects of the present invention will appear from the following description thereof, which will be made with reference to the accompanying drawing, the single figure thereof representing a schematic flow diagram of one mode of practicing the invention.

The present invention provides an improved method for converting alkyl substituted aromatic hydrocarbons having at least one unsubstituted nuclear carbon atom, into diarylmethanes in high yield with high selectivity by condensation with formaldehyde in a process suitable for commercial use. Briefly, the present invention provides a process for the production of diarylmethanes by contacting formaldehyde with a suitable aromatic hydrocarbon feed in a slurry including a finely divided, porous, solid acidic catalyst, while maintaining a high effective ratio of feed aromatic to formaldehyde and a short contact time by introducing formaldehyde into the liquid at a controlled rate to maintain the reaction time at a low value, e. g., less than 15 seconds, continuously withdrawing from the reaction zone a vapor stream containing the water added and that formed in the reaction, and recovering diarylmethanes from the reaction mass.

Suitable hydrocarbon feed stocks for the present invention are alkyl substituted monocyclic aromatic hydrocarbons containing at least one unsubstituted nuclear carbon atom. The reactivity of aromatic hydrocarbons with formaldehyde under the conditions of the present invention increase with the increasing number of alkyl substituents in the ring. Benzene is not readily converted to diphenylmethane according to the present invention. Monocyclic alkyl aromatic hydrocarbons containing at least one unsubstituted nuclear carbon atom, and having no more than six carbon atoms in any one alkyl group and no more than 15 carbon atoms per molecule are preferred feed stocks. Especially preferred feed stocks are the mono- to penta-methylbenzenes, namely: toluene; the xylenes, either as the individual isomers, particularly

ortho- and meta-xylene, or as mixed xylenes, including para-xylene; the trimethylbenzenes, either as the individual isomers hemimellitene, pseudocumene and mesitylene or as a mixture of the isomers; the tetramethylbenzenes, either as the individual isomers particularly prehnitene and isodurene or as a mixture of the isomers, including durene; and pentamethylbenzene. Generally preferred as aromatic hydrocarbon feeds in the present invention are toluene, mixed xylenes, and pseudocumene.

Aromatics having alkyl substituents other than methyl groups can be employed as feed stocks for the present invention, including, for example, ethylbenzene, ethyltoluenes, ethylxylenes, diethylbenzenes, cumene, isopropyl toluenes, isopropylxylenes, and the like.

Generally it is desirable to employ the aromatic hydrocarbon feed stock as a relatively pure fraction of a single molecular weight range, e. g., a concentrate of toluene, of xylenes, of trimethyl benzenes are the like. When employing such fractions, the resulting diarylmethanes are substantially of a single molecular weight range and are very suitable for further conversion, e. g., by hydrocracking, into one aromatic compound corresponding to the feed and another corresponding to the feed aromatic having a methyl group added to the aromatic nucleus. The present invention can be also employed, however, for producing mixed diarylmethanes from a hydrocarbon feed stock containing aromatic hydrocarbons of different molecular weights.

The condensation products produced according to the present invention are suitable for use as high boiling aromatic solvents, as charge stocks to a hydrocracking step to produce methylated aromatics, or as intermediates in the production of insecticides or of wetting agents.

The diarylmethane compounds resulting from the use of toluene, mixed xylenes, pseudocumene, mesitylene and mixed tetramethylbenzenes as feed stocks are suitably hydrocracked in accordance with the method described in patent application Serial No. 399,570 of L. C. Fetterly, filed December 21, 1953, to produce, respectively, in substantial yield paraxylene, pseudocumene, durene, isodurene and pentamethylbenzene.

It is important in the present invention that the formaldehyde be added to the slurry comprising aromatic hydrocarbon feed and suspended catalyst at a controlled rate such that the amount of monomeric formaldehyde entering the liquid phase at any one time is no more than can be substantially completely reacted with the aromatic in a very short period. It is, therefore, preferred to add the formaldehyde in the form of formaldehyde monomer, either anhydrous or aqueous, at a controlled rate. When non-aqueous monomeric formaldehyde is used, it may be charged to the reaction zone as a gas or in solution in organic liquid, e. g., in part of the aromatic hydrocarbon feed stock. The aqueous formaldehyde may be charged as a liquid or a vapor stream.

The prior art workers have generally found the use of aqueous formaldehyde, such as formalin, to be undesirable in the production of diarylmethanes because of the large amount of water thus added to the reaction zone, which dilutes and deactivates the catalysts employed by the prior art in the production of diarylmethanes. In operating according to the present invention, aqueous formaldehyde solution such as formalin is the preferred form in which to charge the formaldehyde to the reaction zone. The solution may contain from 1% to 60%, by weight, or more of formaldehyde. A concentration between 30% and 50% is preferred, commercial formalin of about 37% formaldehyde content being especially suitable.

The catalysts suitable for use in the present invention are solid catalysts of substantial porosity and acidity.

The catalysts are preferably employed in finely divided form, in the manner described below.

A particularly suitable catalyst for use in the present process consists of silica gel containing adsorbed thereon sulfuric acid in an amount ranging between 0.1% and 15% by weight, based on the support. A preferred concentration of sulfuric acid on the silica gel is between 0.4% and 2.5% by weight the range between 0.5% and 1% by weight being especially suitable. The correlation between the amount of sulfuric acid deposited on silica gel and the activity of the catalyst is illustrated in Table I, in which the formaldehyde conversion obtainable with a fresh catalyst is shown for silica gel containing various amounts of sulfuric acid deposited thereon.

TABLE I

Amount of H ₂ SO ₄ , percent weight, on gel	0	0.1	0.5	2.5	5	10	15	30
	Formaldehyde conversion, percent							
Hydrocarbon feed:								
Xylenes (mixed)	~5	30	87	94	92	93	90	---
Pseudocumene	---	---	---	95	96	92	---	---
Toluene	---	---	---	---	55	---	---	10

These results were obtained with the respective identified hydrocarbon feed stocks under conditions which were substantially identical for any one feed stock. The formaldehyde was employed in the form of 37% aqueous formalin. It is apparent that formaldehyde conversion is highest with catalysts having between 0.5 and 10% H₂SO₄ on the silica gel. It was also observed, however, as illustrated in Table II, that at concentrations in the lower part of the effective range, e. g., at 0.5%, the catalyst life, before regeneration, was substantially greater than at the higher concentrations, e. g., between 5 and 10%. It is, therefore, preferred to operate with catalysts having an acid concentration on the silica gel in the lower part of the effective range.

TABLE II

Catalyst life, gms. alkylate per gm. catalyst	2	6	10	12	14	16	20	25
	Formaldehyde conversion, percent							
Amount of H ₂ SO ₄ , percent weight, on gel:								
0.5	88	82	80	78	75	73	66	40
2.5	90	91	90	89	82	58	---	---
5	90	90	60	17	---	---	---	---
10	93	94	26	---	---	---	---	---
15	92	30	---	---	---	---	---	---

The sulfuric acid-on-silica gel catalyst is simply prepared by spraying dry silica gel with the desired amount of an aqueous solution of sulfuric acid. It is preferred to use a relatively dilute acid solution in order to permit even application of the acid to the gel. Use of a solution of 1% to 10% by weight H₂SO₄ is therefore preferred, a strength of about 5% wt. being very suitable. If the amount of water added to the gel by spraying with aqueous acid does not exceed about 30% by weight, the gel may be directly used in the alkylation step. If more water is employed, the gel should be dried before use, e. g., by heating at 150° C. for one hour or more.

Another suitable catalyst for use in the present process is a calcined composite of silica gel containing a small amount of alumina. Such a catalyst also has very substantial acidity. Useful concentrations of alumina, based on the silica gel, range between 0.1 and 15%, the more suitable range being between 0.1 and 5% and the preferred range between 0.5 and 4% of alumina. The formaldehyde conversion obtainable with fresh catalysts of this type is shown in Table III for concentrations of alumina between 0 and 100%, based on the total catalyst. These results were obtained with the respective identified hydro-

carbon feed stocks and 37% aqueous formaldehyde under similar conditions. It is apparent that the obtainable conversion increases drastically between 0 and 0.5% Al₂O₃, increases further to 3.4% Al₂O₃, and decreases greatly with further increases in the concentration of alumina on the catalyst.

TABLE III

Amount of Al ₂ O ₃ , percent weight, on gel	0	0.5	3.4	13	25	100
	Formaldehyde conversion, percent					
Hydrocarbon feed:						
Xylenes (mixed)	~5	75	83.5	67.5	54	0
Pseudocumene	---	---	---	---	---	---

A preferred alumina-on-silica gel catalyst for the present process is prepared by depositing the required amount of alumina in the form of an aqueous solution of aluminum nitrate on silica gel, followed by heating at a temperature between 400° and 700° C. for from 2 to 48 hours, the shorter times being used at the higher temperatures. Temperatures between 550° and 600° C. and times from 2 to 24 hours are preferred, but heating at 500° C. for at least 2 hours is generally sufficient.

A silica-alumina catalyst prepared in the conventional manner, e. g., a cracking catalyst prepared in the manner described in U. S. Patent No. 2,411,820 to Asheley et al., is suitable for use in the present invention, provided it is first subjected to a careful calcination treatment by heating at the above stated conditions. Without such calcination, a conventional cracking catalyst is entirely inactive. Even when calcined, a catalyst containing more than about 5% by weight Al₂O₃ is less active than one having from 0.5 to 5% by weight Al₂O₃.

The solid acidic catalysts found effective in the process of the present invention have in common a relatively high surface area and porosity, a pronounced amount of acidity (as measured by titration with an organic base), and a substantial absence of acid sites having an acid strength as great as that of concentrated liquid sulfuric acid (as measured by means of appropriate indicators).

The surface area and porosity of porous solids usually are related, the solids of highest surface area having the smaller pore sizes. Thus, catalyst having a surface area between 500 and 800 or more square meters per gram and average pore diameters between 20 and 50 Angstrom units have been found particularly useful in the present process, while those of lower surface area, between 100 and 500 m.²/gm., having an average pore diameter between 50 and 100 or more A., were generally less active, but still useful with the more reactive feed stocks.

In order to be effective, the catalyst surface must be acidic, but not excessively so. The preferred catalysts consist of silica gel of the preferred surface and porosity, having deposited thereon no more than one half the amount equivalent to a monomolecular layer of a polybasic mineral acid, which is substantially non-volatile at the reaction conditions, e. g., H₂SO₄, H₃PO₄ or phosphotungstic acid. It is estimated that 30% by weight H₂SO₄ on a silica gel of 800 m.²/gm. surface area corresponds to a monomolecular layer. When an amount of normally liquid mineral acid in excess of a monomolecular layer is employed, e. g., over 30% H₂SO₄ based on silica gel, the excess amount of acid acts like the concentrated mineral acid itself, e. g., like a catalyst of liquid H₂SO₄, as indicated by the fact that the catalyst contains a substantial amount of acidity having a pK_A in excess of -8. (A pK_A of -8 corresponds to a liquid sulfuric acid of about 90% concentration; pK_A of -9 corresponds to 97% H₂SO₄.) A solid catalyst of such strong acidity is unsuitable for use in the present process.

A small amount of Al₂O₃ deposited on silica gel has been found to have acid characteristics similar to a min-

eral acid, and therefore such catalysts also are suitable for use in the present process.

If any of the above catalysts become contaminated by carbonaceous deposits during the course of the reaction they are readily regenerated by a conventional oxidative regeneration, e. g., by burning the catalyst with a gas containing a controlled amount of free oxygen, such as air. If part or all of the mineral acid, such as sulfuric acid, is lost from the silica gel during regeneration, it is replaced before reuse of the catalyst.

The present reaction is carried out in the liquid phase. In the preferred method of operation, an agitated slurry comprising the catalyst particles suspended in a liquid body comprising aromatic hydrocarbon charge stock and, generally, some product, is maintained in a heated reaction zone at a temperature sufficiently high to permit prompt removal of all water added to and formed in the reaction zone in the form of a vapor stream comprising the water and some of the charge hydrocarbon. Aqueous or anhydrous formaldehyde is gradually added to the reaction zone; any water which is added with the formaldehyde, together with the water formed in the reaction, is immediately removed from the reaction zone by continuously withdrawing vapors of water and aromatic. The vapors withdrawn from the reaction zone are condensed; the aromatic hydrocarbon is suitably returned to the reaction zone. If unreacted formaldehyde is removed in the vapor stream, it will be contained in the water layer of the condensate; such recovered formaldehyde may also be returned to the reaction zone.

The reaction can be carried out in a batchwise operation by placing a desired amount of the aromatic hydrocarbon in the reaction zone together with the required amount of catalyst, agitating and heating, and gradually adding sufficient formaldehyde to produce the desired amount of the diarylmethane. In the continuous method of operation, a body of liquid comprising catalyst slurried in aromatic charge hydrocarbon and product is maintained in the reaction zone, fresh aromatic hydrocarbon charge and formaldehyde are continually added and a bleed stream of the liquid is continually withdrawn for recovery of product therefrom.

The temperature employed in the present reaction is at least sufficiently high to permit continuous evaporation of water from the reaction zone substantially at the rate at which it is added and formed. Temperatures between 100° C. and 200° C. are preferred, though temperatures up to 250° C. may be employed. Temperatures between 115° and 165° C. are most suitable. Preferably the temperature is near, but below, the boiling point of the aromatic hydrocarbon feed or the initial boiling point of an aromatic feed mixture. It may be slightly higher than the initial boiling point, but should be below the point where substantial ebullition takes place. Preferred ranges for compounds boiling up to about 185° are within 20° C. of the boiling point of a pure aromatic hydrocarbon feed or the initial boiling point of a mixed aromatic hydrocarbon feed, at the pressure prevailing in the system.

Atmospheric pressure is preferably employed in the process of the present invention. At times it may be desirable to employ somewhat higher pressures to permit operation at higher temperatures, particularly with a relative low boiling hydrocarbon, such as toluene. Thus, pressures from 1 to 10 atmospheres are suitably employed, while a pressure of from 1 to 3 atmospheres is generally preferred.

With the preferred hydrocarbon feed stocks and catalysts the condensation reaction between the aromatic hydrocarbon and formaldehyde according to the present invention is a very nearly instantaneous reaction. The reaction is ordinarily substantially complete within 2 to 5 seconds after the addition of an increment of monomeric formaldehyde to a body of aromatic hydrocarbon. The rate of addition of formaldehyde is controlled such

that no more formaldehyde is added to a reaction mixture at any time than can be substantially completely converted to condensation product within a very short time. This time should be less than 1 minute and is preferably less than 15 seconds and in the most preferred case is no more than 5 seconds.

For any given system of reagents, catalyst and reactor arrangement, the maximum increment of formaldehyde which may be added to the reactor at any one time in order to be completely reacted within a given time, e. g., 5 seconds, is readily determined by maintaining the reactor system at operating conditions without addition of formaldehyde, then instantaneously adding a desired increment of formaldehyde and at the proper time, e. g., 5 seconds after the addition of the increment, withdrawing a sample of the liquid mixture from the reactor. The reaction in the withdrawn sample is immediately quenched, e. g., by cooling and removing catalyst from the liquid, and the amount of conversion of formaldehyde may be determined by analyzing for diarylmethane and higher condensation products in the sample. In a continuous system operating with continuous addition of formaldehyde and feed aromatic and continuous withdrawal of a bleed stream of liquid and a vapor stream, as described, the formaldehyde addition is suitably controlled by continually analyzing the condensate from the vapor stream for formaldehyde content and reducing the addition rate of fresh formaldehyde when the formaldehyde content of the vapor stream begins to increase from the steady state value. When operating under the conditions of the present invention, no substantial concentration of unconverted formaldehyde builds up in the liquid reaction mass.

The ratio of feed aromatic hydrocarbon to unreacted formaldehyde monomer in the reaction slurry is desirably very high, e. g., from 30 to 2000 moles of aromatic per mole of formaldehyde. Although ratios as low as about 12:1 have been successfully employed when a relatively large increment of formaldehyde was added at one time, it is preferred, for best results, to maintain the ratio in the range between 100 and 2000:1 by continuous addition of formaldehyde, i. e., adding formaldehyde in small increments.

In batch operation, the ultimate ratio of feed aromatic to formaldehyde is maintained substantially in excess of the stoichiometric mole ratio of 2:1. It may be in the range between 3:1 and 20:1 and is preferably between 4:1 and 7:1. Aldehyde addition, in a batch reaction, is discontinued when the concentration of condensation product in the liquid has reached 60% by weight, or earlier.

In a continuous reaction system the composition of the steady state reaction mixture is controlled to maintain in the liquid no more than 60% by weight of condensation product, i. e., diarylmethanes and higher, and preferably a proportion of condensation products below 50% and desirably as low as 5 to 20%. Since the liquid consists substantially entirely of aromatic feed and product, the concentration of feed in the steady state reaction liquid is desirably between 40% and 95% by weight.

The amount of catalyst maintained in the reaction zone is in the range between 1 and 30 weight percent or more, based on the liquid content of the slurry, and preferably between 10 and 20 weight percent of the liquid in the reaction zone. The bulk density of the dry powdered catalysts suitable for use in the present invention is generally about the same as the density of the aromatic feed or the liquid reaction mass. Hence, the ratio of aromatics to catalyst expressed as parts by weight is approximately equal to the ratio expressed in parts by volume, employing the dry bulk volume of the catalyst.

In numerous runs carried out in accordance with the present invention it has been found that the amount of aromatic hydrocarbon feed reacted was substantially

entirely converted to condensation product with formaldehyde, i. e., to the extent of 98% or better. In contrast, the method for producing diarylmethane according to the prior art generally involves the use of strong liquid acid catalysts, e. g., concentrated sulfuric acid, and in these reactions a substantial proportion of feed aromatic is lost to undesired by-product other than condensation compounds with formaldehyde.

With minor exceptions, the condensation product obtained in runs carried out in accordance with the present invention consisted of at least 85% and generally between 90 and 100% of the diarylmethanes, the remainder being mainly triaryldimethanes and sometimes small amounts of the tetra-aryltrimethanes or higher compounds. Substantially no resins are produced in the reaction according to the present method.

Thus, in converting, according to the present invention, feeds consisting essentially of toluene, meta-xylene, pseudocumenes, mesitylene, or mixed tetramethylbenzenes, respectively, the product in each case contained between 85% and 100% of the respective diarylmethanes. With paraxylene and durene it was found that the product contained only about 70% of the diarylmethane, the remainder being triaryldimethane and some higher condensation product. It appears, therefore, that in the present process, the selectivity to the diarylmethane compounds is higher for those alkyl aromatics which have open a para-position opposite to an existing alkyl substituent. Representative product distributions are given in Table IV.

TABLE IV

Product distribution in formaldehyde alkylation of methylbenzenes

Aromatic reactant	Catalyst	Percent mole		
		Diaryl-meth-ane	Triaryl-dimeth-ane	Heav-ier, as tetra-aryltri-meth-ane
Toluene.....	1% H ₂ SO ₄ /silica-gel..	96	4	0
Mixed xylenes (mainly meta). Do.....	5% H ₂ SO ₄ /silica-gel..	100	0	0
p-Xylene.....	3.4% Al ₂ O ₃ /silica-gel..	96	4	0
Mesitylene.....	10% H ₂ SO ₄ /silica-gel..	67	19	14
Pseudocumene ²	do.....	89	11	0
Durene.....	1-10% H ₂ SO ₄ /silica-gel..	85	15	0
Mixed tetramethylbenzenes: 34% prehnitene.....	10% H ₂ SO ₄ /silica-gel..	69	31	0
41.5% isodurene.....	do.....	92	8	0
24.5% durene.....	do.....			

¹ All material heavier than diarylmethane calculate as triaryldimethane (based on molecular weight analyses).

² Average of several runs.

The process of the present invention will be further described by means of the sole figure of the drawing, which is a schematic flow sheet of a preferred method of operation. When the process is operating continuously, aromatic feed hydrocarbon is charged to the system through line 11. Formaldehyde, preferably in aqueous solution, e. g., 37% aqueous formalin, is charged through line 12. Both these streams enter the reactor 14, in which there is maintained a volume of slurry 15 and a vapor space 16. The slurry 15 contains suspended therein finely divided catalyst, e. g., 10 weight percent of silica gel containing 1% by weight sulfuric acid (based on the gel). This suspension of catalyst in the liquid is maintained by stirrer 18, driven by prime mover 19. The condensation reaction is exothermic, but further heat is required to evaporate water and other material removed in the vapor stream described below. It is preferred to supply this heat by

means of the vapor overhead stream from distillation column 31, which enters reactor 14 via line 35. Alternatively, all or part of the required heat may be supplied by heat exchange means 20, which represents a steam coil or a reactor jacket or other suitable heat exchange means. When the heat in the vapor stream from column 31 exceeds the required amount, heat exchanger 20 may operate as a cooling means. Valved drawoff line 21 is provided for draining the reactor, e. g., for periodic removal of spent catalyst and replacement thereof by fresh catalyst.

A vapor stream is withdrawn continuously from the vapor space of the reactor through line 22, containing condenser 24, and the condensed vapor stream is passed to separator 25 from which there is withdrawn an aqueous stream through line 26 and a hydrocarbon stream through line 28. The hydrocarbon stream in line 28 may be withdrawn through line 29 but is preferably returned to line 11. The aqueous stream in line 26 may contain a substantial amount of formaldehyde and may be worked up for reuse of the formaldehyde, e. g., by vaporizing the formaldehyde and recycling the vapor stream. The formaldehyde content of the aqueous streams is a function of the completeness of formaldehyde conversion in reactor 14, which, in turn, is determined by the reactivity of the hydrocarbon charge compound, the catalyst activity, and other factors, such as temperature, which affect the reaction rate and completeness of reaction, as well as by the rate of addition of formaldehyde to the reaction zone. At the preferred reaction conditions, the stream in line 26 is substantially free of formaldehyde.

A portion of the liquid of slurry 15 is continually withdrawn from reactor 14 through line 30, whose inlet may be protected by a settling zone or a filter or similar means to avoid withdrawing solid catalyst particles from the reactor. The liquid stream in line 30, comprising a portion of the steady state reaction mixture, is passed to distillation column 31, which is equipped with internal or external reboiling means 37 and internal or external condensing means 33. The rate of withdrawal of liquid through line 30 and the operation of column 31 are preferably so controlled that the uncondensed portion of the column overhead returned to reactor 14 via lines 32 and 35 is sufficient to supply essentially all the heat requirements in the reactor. In such operation, condenser 33 operates as a partial condenser to supply liquid reflux to column 31 and permit withdrawal of the remaining overhead stream as hot vapor. The overhead stream withdrawn through line 32 comprises essentially unconverted feed aromatic hydrocarbon. Part or all of the overhead stream may be withdrawn from the system through valved line 34 but it is preferably returned to reactor 14 via line 35. The desired product of the reaction, generally the diarylmethane, is withdrawn from column 31 through line 36, and may be further purified by means not shown. This stream may contain some feed hydrocarbon. Product heavier than the diarylmethane, which may be formed in a small amount in the process, may be withdrawn through line 38. If desired, however, both diarylmethane and triaryldimethane may be withdrawn together as combined product of the reaction. The product withdrawn through line 36, either the diarylmethane or the mixed diarylmethane and triaryldimethane, is a suitable chemical intermediate in the production of aromatics containing one more methyl group than the feed aromatic. It may be hydrocracked in accordance with the method described in the above mentioned patent application Serial No. 399,570, to produce a mixture of methylated feed aromatic and unchanged feed aromatic, and the latter may be returned for further reaction in the present process.

Numerous details of the equipment such as pumps, valves, instruments and the like, have been omitted from the drawing and description. The placement of such

components will be readily apparent to the persons skilled in the art.

Although reactor 14 is shown as a stirred reactor, the suspension of catalyst in the liquid may be maintained by other equivalent means, e. g., by the injection of fluid into the bottom of the reactor at such a rate that a suspension is maintained.

In an example of operation according to the method described in connection with the drawing, the hydrocarbon charged through line 11 is pseudocumene and the formaldehyde is charged through line 12 in the form of 37% aqueous formalin. The liquid slurry 15 contains 1000 pounds of liquid of which 800 pounds is pseudocumene and 200 pounds is essentially dipseudocumylmethane. The slurry also contains 100 pounds of a catalyst of highly porous silica gel containing 5% by weight of sulfuric acid. Pseudocumene is added through line 11 at the rate of 600 pounds per hour (5 pound mols) and formalin through line 12 at the rate of 206 pounds per hour (2.5 pound mols of formaldehyde). In order to maintain the desired ratio of pseudocumene to dipseudocumylmethane in the reaction liquid, it is necessary to remove 635 pounds per hour of dipseudocumylmethane (2.5 pound mols). The liquid bleed stream in line 30, therefore, is withdrawn at the rate of 3,175 pounds per hour of which 635 pounds per hour is dipseudocumylmethane which is withdrawn from the system through line 36 and 2,540 pounds per hour is pseudocumene which is returned to the reactor as vapor through line 35. The vapor stream withdrawn from the reactor through line 22 contains 126 pounds per hour of water introduced with the formalin, 45 pounds per hour of water produced in the reaction, and approximately 1,200 pounds per hour of pseudocumene; the latter is ultimately returned through line 28, the water being discarded through line 26.

Modifications of the reaction system described by means of the drawing may be employed without departing from the scope of the present invention. Thus, in order to maintain the desired high ratio of aromatic feed hydrocarbon to formaldehyde in the reaction mixture, the formaldehyde may be injected at two or more separate points within the reactor. In a similar modification, two reactors are employed, the reaction liquid flowing from one to the other in series and formaldehyde being injected separately into each reactor.

The catalyst gradually loses activity in the above described operations, generally over a period of from 5 to 10 hours. The so deactivated catalyst may be regenerated by separating it from the reaction mass, burning off all carbonaceous material, if necessary replenishing the acid content to the desired value and, returning the catalyst to the reactor. In a preferred operation a portion of the slurry is continuously withdrawn from the reactor, the catalyst separated therefrom by filtration or settling, and the so separated portion of catalyst is regenerated and returned to the reactor or is replaced by fresh catalyst.

The invention will be further described by means of the following illustrative examples:

EXAMPLE I

A batch reaction in accordance with the present invention was carried out in a vessel equipped with a stirrer for the liquid zone, an inlet line for addition of aqueous formaldehyde solution and an outlet from the vapor phase zone leading to a condenser and phase separator vessel. Twenty parts by volume of a catalyst consisting of 5% H_2SO_4 supported on 28 to 200 mesh particles of silica gel of 750-800 square meter per gram surface area was placed in the reaction vessel. One hundred parts by volume of a mixture of xylenes, containing 4% ethylbenzene and 28% para-, 63% meta-, and 5% ortho-xylene, was also placed in the vessel. In addition, 16 parts by volume of the mixed xylenes fraction was placed in the phase separator vessel. The liquid in the reaction vessel was stirred and the resulting slurry heated by an

external heating jacket to a temperature of 135° C. After reflux of the aromatic hydrocarbon from the condenser was established, 10 parts by volume of 37% liquid aqueous formalin was added in small increments to the vessel at a rate slightly below that which would cause boiling of the mixture from the top of the condenser. The addition of formalin was completed in 30 minutes, the reaction temperature being maintained at 130°-135° C. during the addition and the mixture being continuously stirred so as to maintain the solid catalyst in suspension. The aqueous portion of the material taken overhead was continuously condensed and withdrawn from the phase separator. After addition of formalin was completed, heating and stirring were discontinued and the catalyst allowed to settle, after which the liquid product mixture was withdrawn from the vessel by decantation. The degree of aldehyde conversion was determined by analyzing for unreacted aldehyde withdrawn in the aqueous phase and in the liquid product.

The product was worked up by batch distillation in which, first, unconverted formaldehyde was taken overhead, then unconverted xylene mixture, and finally the dixylylmethanes.

It was found that 90 mole percent of the formaldehyde added and 30 mole percent of the mixed xylenes had been converted to useful product.

The product recovered had the following characteristics:

Total product:		Percent weight
Xylene fraction-----		68
Ethyl benzene-----	5	
Paraxylene -----	25	
Metaxylene -----	36	
Orthoxylene -----	2	
Diarylmethane -----	32	
Triaryldimethane -----	0	
		100
Alkylate:		
Molecular weight of alkylate fraction----	222	
Percent diarylmethane-----	100	

EXAMPLE II

In a manner similar to that described in Example I a number of runs were made in which a number of different aromatic hydrocarbon feeds were reacted with aqueous formalin of 37% concentration. Operating conditions and results of these runs are given in Table V. Component analyses of mixed hydrocarbon feeds are shown in Table V-A. In all of these runs the catalyst employed consisted of sulfuric acid supported on silica gel of high surface area and small pore size.

The data in Table V illustrate the reactivity of a variety of aromatic hydrocarbons when employing finely divided solid porous acidic catalysts of H_2SO_4 on silica gel and operating in accordance with the conditions of the present invention.

The residence time of the formaldehyde in the reaction zone in the present invention is relatively short since formaldehyde tends to be taken overhead with the stream of aromatics and water vapor leaving the reactor. Hence, in order to obtain complete aldehyde conversion the reaction time between the formaldehyde and the aromatic hydrocarbon must be very short. It is illustrated in Example IV that this time is less than six seconds and that conversion is 75% complete in 2 seconds with a system of mixed xylenes, 37% formalin and a silica gel catalyst containing 1% H_2SO_4 . Therefore, the percent of formaldehyde conversion of the various hydrocarbons in Table V, other conditions being equal, illustrates the reactivity of the hydrocarbon. Thus, toluene at up to 103° C. and para-xylene at up to 136° C. are relatively less reactive than mixed xylenes, mixed trimethyl benzenes and mixed and individual tetramethyl benzenes. The relatively lower conversion obtained in run 7 with

TABLE V

Run No.	Catalyst	Feed aromatic	Boiling point or range, ° C.	Ultimate molar ratio	Reaction temperature, ° C.	Time for formalin addition, min.	Volume ratio aromatics: catalyst	Conversion of formaldehyde, percent	Condensation product		
									Diarylmethane, percent	Triaryldimethane, percent	Heavier (as tetraaryltrimethane), percent
1	Silica gel+10% wt. H ₂ SO ₄	Toluene	110.6	7.1/1	99-103	30	5/1	63			
2	do	Paraxylene	138.4	4.0/1	134-136	87	5/1	63	67	19	14
3	do	Xylenes ^a	136.2-144	6.1/1	132-137	84	10/1	94			
4	Silica gel+5% wt. H ₂ SO ₄	do	136.2-144	6.1/1	133-138	55	5/1	90	100	0	0
5	Silica gel+10% wt. H ₂ SO ₄	Trimethylbenzenes ^a	162-176.5	5.5/1	150-160	34	5/1	92			
6	Silica gel+1% wt. H ₂ SO ₄	do	162-176.5	5.4/1	160-164	35	10/1	76	97	^b 3	
7	Silica gel+10% wt. H ₂ SO ₄	Mesitylene (99%)	164.6	2.7/1	150-158	105	6/1	78	89	^b 11	
8	do	Durene (>95%)	193.5	4.7/1	155-160	59	ca. 5/1	96			
9	do	Prehnitene (>90%)	204	1.9/1	148-160	103	5/1	89			
10	do	Tetramethylbenzenes ^a	193-204	3.3/1	155-158	162	5.5/1	93			

^a Details in Table V-A.^b Total heavier than diarylmethane, calculated as triaryldimethane.

TABLE V-A

Aromatic feed compositions (percent)

Run No.	3, 4	5	6	10
Aromatic:				
Ethylbenzene	4			
Orthoxylene (1,2-dimethylbenzene)	5			
Metaxylene (1,3-dimethylbenzene)	63			
Paraxylene (1,4-dimethylbenzene)	28			
Hemimellitene (1,2,3-trimethylbenzene)		<3		
Pseudocumene (1,3,4-trimethylbenzene)		79	83	
Mesitylene (1,3,5-trimethylbenzene)		<18		
Orthoethyltoluene (1-ethyl-2-methylbenzene)		3		
Prehnitene (1,2,3,4-tetramethylbenzene)				34
Isodurene (1,2,3,5-tetramethylbenzene)				42
Durene (1,2,4,5-tetramethylbenzene)				24

mesitylene may be explained by the relatively low ultimate ratio of aromatics to aldehyde, meaning that a larger amount of formaldehyde was charged to a given volume of aromatics in the reactor, hence permitting a greater loss of aldehyde in the vapor effluent.

With most of the aromatics feeds, under the conditions illustrated, the alkylate produced contained between 90 and 100% of the diarylmethane. An exception is paraxylene, the produce containing 67% diarylmethanes, 19% triaryldimethanes and 14% heavier material. This is believed to be a characteristic of those aromatic hydrocarbons having no open para position in the aromatic ring, which are less selectively converted to the diarylmethane than those aromatic hydrocarbons that do have an open para position.

In general, it is illustrated that aromatic hydrocarbons having at least one methyl substituent and particularly those having an open para position are readily converted in accordance with the present invention to a product containing a very high proportion of diarylmethane and substantially no resin. The more highly substituted aromatics are more reactive and permit a higher conversion of formaldehyde at a given formaldehyde holdup time in the reaction system. It is also shown that a relatively high ultimate molar ratio of aromatics to aldehyde is conducive to high aldehyde conversion per pass.

EXAMPLE III

As illustrated in Example II, the reactivity of aromatic hydrocarbons with formaldehyde under the conditions of the present invention increases with increasing ring substitution of the aromatic. For aromatics with the same number of substituents in the ring, the reactivity also varies with the arrangement of the alkyl substituents. In order to illustrate the relative reactivity of xylenes, a mixed xylenes feed containing 4.5 mole percent ethyl benzene, 4.7 mole percent ortho-xylene, 27.9 mole percent para-xylene and 62.9 mole percent meta-xylene was reacted with aqueous formalin essentially under the conditions of Example I and at the temperature, ultimate molar

ratio of aromatics to aldehyde, addition time and catalyst-to-aromatic ratio of run No. 4 in Table V. The conversion of formaldehyde obtained was 94% and of the total aromatics feed, 31% by weight (30% mole) was converted to essentially diarylmethanes.

Based on the amount of each of the isomers in the feed to the reaction, it was found that no ethylbenzene had been converted, approximately 37% of the ortho-xylene and approximately 7% of the para-xylene present had been converted, and about 42% of the meta-xylene had been converted to the respective diarylmethanes. The mixed alkylate from this run was segregated and hydrocracked by passage with 2.9 moles of hydrogen per mole of alkylate over a nickel sulfide tungsten sulfide catalyst at a temperature of 450° C. and pressure of 35 atmospheres. The product recovered from the hydrocracking step, in addition to pseudocumene, contained xylene isomers of the following distribution: 1.5% ortho-xylene, 6.3% para-xylene, 91.8% meta-xylene and no ethyl benzene.

This experiment demonstrates the relatively high reactivity of ortho-and especially of meta-xylene when present in a mixture of xylenes, under the conditions of the present invention.

EXAMPLE IV

100 volume parts of an aromatic feed of mixed xylenes comprising 5% ortho-xylene, 4% ethyl benzene, 28% para-xylene and 63% meta-xylene were reacted with 37% aqueous formalin in the presence of 20 volume parts of a catalyst of 1% by weight of H₂SO₄ supported on porous silica gel, in a system substantially like that of Example I. After the system was brought to a reaction temperature of 136° C., two parts by volume of aqueous, 37% formalin were added while the system was being agitated. A sample drawn after 2 seconds showed that 75% of the formaldehyde added had reacted to form, essentially, diarylmethanes. At the end of 6 seconds, 96 to 98% of the formaldehyde had reacted. Ten more parts by volume of the aqueous formalin were then added dropwise over a period of 30 minutes. At the end of that period the conversion of formaldehyde to essentially diarylmethanes was 94% complete. An additional two parts by volume of aqueous formalin were then added in one increment and after approximately 4 seconds another sample was withdrawn and the formaldehyde conversion of the additional increment was shown to be 90 to 91% complete.

In a repetition of a similar experiment, employing pseudocumene as the charge aromatic hydrocarbon and the same type of catalyst, and maintaining a temperature of 160-164° C., essentially identical results were obtained with respect to the rapidity of the completion of the reaction between the added formaldehyde and pseudocumene.

13

EXAMPLE V

The formaldehyde conversions obtainable under conditions similar to those of Example I when employing catalysts of silica gel of high porosity and surface area containing from 0.1% to 30% sulfuric acid deposited thereon are presented in Table I and results obtainable with silica-alumina catalysts in Table III of the present specification. In a similar experiment, toluene was contacted with formaldehyde in the presence of an uncalcined commercial cracking catalyst containing 12% alumina; no formaldehyde was converted under the conditions of the experiment.

In a further similar experiment a silica gel of high surface area and small pore size, containing no acid deposited thereon, was contacted with trimethylbenzene and an aqueous 37% formalin at conditions similar to run No. 5 of Table V and only 6% of formaldehyde conversion was observed, based on the weight percent of alkylated aromatics recovered. The weight balance of formaldehyde for this experiment indicated that some aldehyde was reacted, apparently to form polymers of formaldehyde itself rather than diarylmethanes or higher condensation product.

EXAMPLE VI

For best results in accordance with the present invention it is important that the solid acidic catalyst employed be highly porous, having a high surface area and relatively small pore size. In order to illustrate this effect, two runs were carried out in which mixed xylenes feed, at otherwise identical conditions of ratio of aromatics to aldehyde, temperature and the like, except for addition time, specified below, was contacted, in one case, with a catalyst consisting of 0.5% weight H_2SO_4 on a silica gel having a surface area of 800 square meter/gram and average pore diameter of 24 A. and, in the other case, with a similar catalyst having a surface area of 300 to 400 square meter/gram and average pore diameter of 80 to 100 A. The aldehyde addition time for the former, highly porous catalyst was 22 minutes and for the latter, moderately porous catalyst 62 minutes, thus favoring increased aldehyde conversion in the latter case. The formaldehyde conversion observed with the former catalyst was 89% and with the latter catalyst, 47%.

EXAMPLE VII

Although sulfuric acid is the preferred mineral acid for use on a porous solid support in the present invention, other mineral acids are suitably employed, supported on a porous carrier, in the present reaction. For example, under otherwise identical conditions similar to Example I, toluene and 37% aqueous formalin were reacted with a catalyst consisting in one case of 10 wt. percent sulfuric acid on highly porous silica gel and in the other case of 10 wt. percent phospho-tungstic acid on identical silica gel. Aldehyde conversions obtained were 55% and 58%, respectively, thus demonstrating substantially identical activity in these catalysts.

In another experiment, mixed xylenes and 37% aqueous formalin were reacted in the presence of a catalyst, in one case, of 10 wt. percent sulfuric acid on highly porous silica gel, and, in the other case, of 10 wt. percent phosphoric acid on highly porous silica gel. It was found that with the sulfuric acid catalyst, formaldehyde conversion obtained was 84%, and with the phosphoric acid catalyst, 63%, thus demonstrating substantial activity in the silica gel supported phosphoric acid catalyst.

We claim as our invention:

1. A process which comprises maintaining in a reaction zone a slurry comprising, in an organic liquid phase, an aromatic feed hydrocarbon having at least one alkyl substituent and at least one unsubstituted nuclear carbon atom and no more than 60% by weight of condensation product of said feed aromatic and formaldehyde and a finely divided porous solid acidic catalyst, at a tempera-

14

ture at which water and feed aromatic are vaporized from said reaction zone, continually adding to said reaction zone a stream comprising said feed aromatic hydrocarbon and a stream comprising monomeric formaldehyde, continuously withdrawing from said reaction zone a vapor stream comprising feed aromatic hydrocarbon and water, condensing said vapor stream, separating a liquid hydrocarbon phase from said condensed vapor stream and returning it to said reaction zone, withdrawing a liquid bleed stream from said reaction zone, subjecting said liquid bleed stream to distillation in a distillation zone, withdrawing therefrom a vapor stream comprising essentially feed aromatic hydrocarbon, returning said vapor stream to said reaction zone to supply heat of reaction thereto, and withdrawing at least diarylmethane as product from said distillation zone.

2. A process according to claim 1 in which aqueous formaldehyde is added at a rate controlled so that no more than an amount of monomeric formaldehyde capable of reacting substantially completely with said feed aromatic within 15 seconds is present in said slurry.

3. A process according to claim 1 in which the feed aromatic hydrocarbon is a mononuclear aromatic having from one to five methyl substituents.

4. A process according to claim 1 in which the feed aromatic hydrocarbon is toluene.

5. A process according to claim 1 in which the feed aromatic hydrocarbon is a mixture of xylene isomers.

6. A process according to claim 1 in which the feed aromatic hydrocarbon is pseudocumene.

7. A process according to claim 1 in which the feed aromatic hydrocarbon is mesitylene.

8. A process according to claim 1 in which the feed aromatic hydrocarbon is a mixture of tetramethylbenzene isomers.

9. A process according to claim 1 in which said catalyst is a calcined solid composite of silica and alumina containing from 0.5 to 5% by weight of alumina.

10. The process according to claim 1 in which said distillation is a fractional distillation.

11. A process which comprises maintaining a reaction mixture comprising an organic liquid phase containing an aromatic feed hydrocarbon having at least one alkyl substituent and at least one unsubstituted nuclear carbon atom and having no more than 15 carbon atoms per molecule and a condensation product of said feed aromatic and formaldehyde and a finely divided porous solid acidic catalyst at a temperature at which water and feed aromatic are vaporized from said reaction mixture, continually adding to said reaction mixture a stream comprising said feed aromatic hydrocarbon and a stream comprising monomeric formaldehyde, continuously withdrawing from said reaction mixture a vapor stream comprising feed aromatic hydrocarbon and water, condensing said vapor stream, separating a liquid hydrocarbon phase from said condensed vapor stream and returning it to said reaction mixture, withdrawing a liquid bleed stream from said reaction mixture, vaporizing the lower boiling portion of said liquid bleed stream, returning the resulting vapor stream comprising essentially feed aromatic hydrocarbon to said reaction mixture to supply heat of reaction thereto, and recovering diarylmethane as product from the unvaporized portion of said bleed stream.

12. A process which comprises maintaining a reaction mixture comprising an organic liquid phase containing an aromatic feed hydrocarbon having at least one alkyl substituent and at least one unsubstituted nuclear carbon atom and a condensation product of said feed aromatic and formaldehyde and a finely-divided porous solid acidic catalyst at a temperature at which water and feed aromatic are vaporized from said reaction mixture, continually adding to said reaction mixture a stream comprising said feed aromatic hydrocarbon and a stream comprising formaldehyde, continuously withdrawing from said reaction mixture a vapor stream comprising feed aromatic hydrocarbon and water, condensing said vapor stream, sep-

15

arating a liquid hydrocarbon phase from said condensed vapor stream and returning it to said reaction mixture, withdrawing a liquid bleed stream from said reaction mixture, recovering unconverted feed aromatic hydrocarbon from said bleed stream and returning it to said reaction mixture and recovering diarylmethane as product from said bleed stream.

2,398,825
2,403,803
2,422,443
2,660,572

5

References Cited in the file of this patent

UNITED STATES PATENTS

2,186,022 Holm et al. _____ Jan. 9, 1940

10

Welch et al.: Jour. Am. Chem. Soc., vol. 73, pp. 4391-3 (1951).

16

Funsten _____ Apr. 23, 1946
Ciapetta _____ Nov. 11, 1947
Smith _____ June 17, 1947
Feasley _____ Nov. 24, 1953

FOREIGN PATENTS

446,450 Great Britain _____ Apr. 30, 1936

OTHER REFERENCES