Fig. 1

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Fig. 2

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Fig. 3

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Fig. 5

SPECIFIC RATE CONSTANT
VS.
MOL. FRACTION CATALYST
FOR
DISPROPORTIONATiON

Fig. 4

SPECIFIC RATE CONSTANT
VS.
MOL. FRACTION CATALYST
FOR
ISOMERIZATION

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The present invention relates to catalytic iso-
merization of aromatic compounds containing a
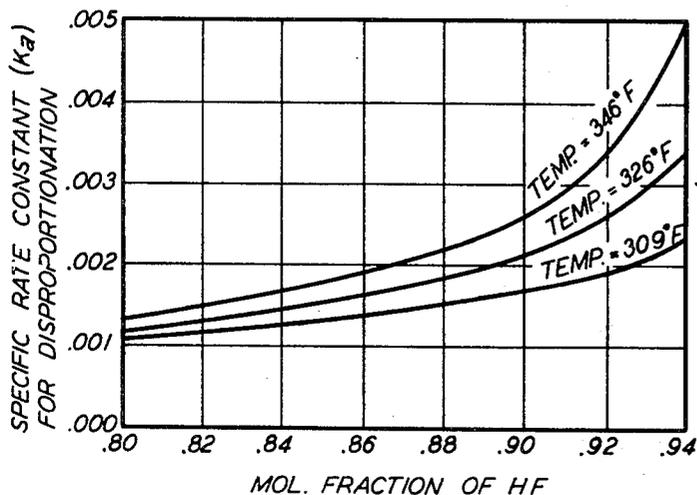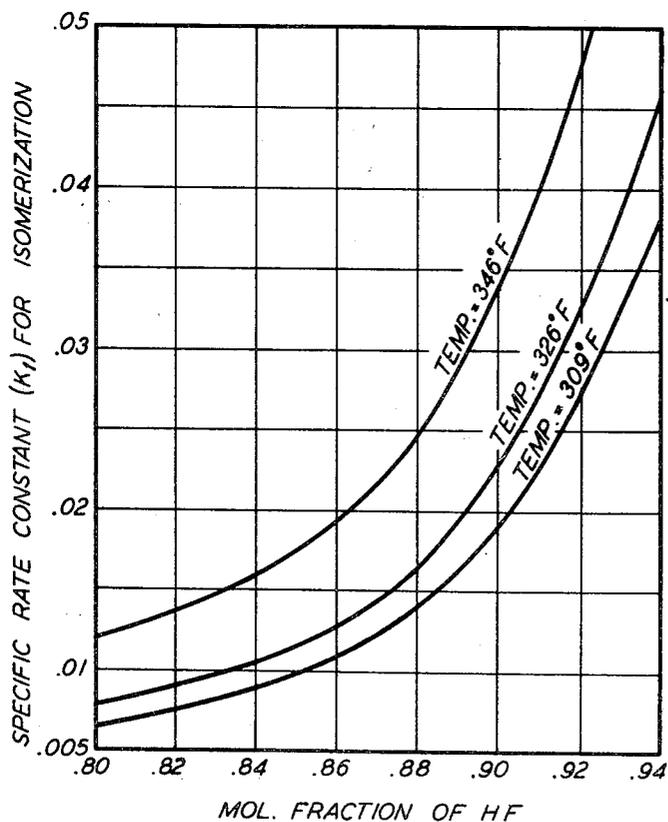plurality of saturated side chains and more par-
ticularly to catalyzing the shifting of intact ali-
phatic groups (preferably without isomerization
of the groups per se) along or around the benzene
ring of an aromatic hydrocarbon. This type of
isomerization of aliphatic-substituted aromatic
compounds involves aliphatic to aromatic carbon
to carbon bonds and is hereinafter termed iso-
merization at the ring or nucleus to distinguish
from mere isomerization of aliphatic to aliphatic
carbon bonds in an aliphatic chain or aromatic
to aromatic carbon bonds in the cyclic structure
of the ring itself.

An object of this invention is to produce com-
mercially valuable isomeric alkyl aromatic com-
pounds from other alkyl aromatic compounds
having the same number of alkyl side chains.

Another object of this invention is the prepa-
ration of para dialkyl benzenes from meta and/or
ortho dialkyl benzenes by an improved process.

A further object of this invention is to provide
a new and improved process and apparatus for
converting a polymethyl benzene to an isomer
thereof and more particularly to isomerize meta
and/or ortho xylenes to para xylene.

An additional object of this invention is to
minimize disproportionation reactions in the iso-
merization of polyalkyl aromatic hydrocarbons.
To furnish an improved method for selectively
catalyzing isomerization while suppressing dis-
proportionation of xylenes comprises another ob-
ject of the invention.

It is also an object simultaneously to eliminate
ethyl benzene and avoid buildup of this impurity
in a cyclic process for isomerization of xylenes
containing ethyl benzene. Another object is to
provide a new and useful reaction technique for
effecting faster conversion of polyalkyl benzenes
by isomerization.

Although the invention is particularly appli-
cable to and finds its greatest present utility in
the isomerization of dialkyl benzenes, more no-
tably dialkyl benzenes in which at least one alkyl
group is methyl, and especially xylenes, the inven-
tion in its broader aspects is applicable to other
alkyl aromatic compounds. However, it has been
found that methyl substituents are more difficult
to isomerize at the aromatic nucleus than are
longer alkyl substituents, and it will be apparent
in the light of the following disclosure that the
invention is applicable to other aliphatic-substi-
tuted aromatics, and more desirably to dialkyl
benzenes containing from 1 to 4 carbon atoms in
each side chain. For the sake of simplicity the
invention will be illustrated primarily by refer-
ence to the more difficult isomerization, i. e., cata-
lyzing the shift of methyl groups at the benzene
ring as in the xylenes.

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Flexibility and economical utilization of alkyl
aromatic hydrocarbons introduce a need for an
efficient process for conversion of alkyl aromatic
compounds from one isomeric form to another.
Thus, orthoxylene is convertible by oxidation to
phthalic anhydride and in some instances it may
become desirable to increase the supply of ortho-
xylene for this or other uses by conversion of
meta or para xylenes. On the other hand, meta
and para xylenes are superior to orthoxylene as
blending agents or additives for certain special
motor fuels, and the supply of this superior blend-
ing agent could be enhanced by isomerization of
orthoxylene. In still another situation, relatively
pure para xylene is developing into an important
chemical for manufacture of various derivatives,
and in those xylene plants which specialize in pro-
duction of the para isomer there is the need of a
suitable process for converting ortho xylene or
meta xylene or both to the para product. Pure
meta xylene (as distinguished from mixtures of
meta and para xylenes for gasoline blending) as
yet has encountered no large market demand,
but flexibility of industrial operations to meet any
future requirements for this isomer makes it de-
sirable to provide a process for isomerization of
ortho or para xylenes or both to the meta isomer.

To appreciate the difficulties in the develop-
ment of a process for isomerizing one or more of
the xylenes, it should be recognized that a large
number of reactions potentially may, and many
actually do, occur simultaneously. One of the
major problems therefore becomes the provision
of a process which will promote selectivity in
effecting the desired isomerization reaction or re-
actions while inhibiting or eliminating formation
of undesired side reaction products. The follow-
ing discussion is in reality an oversimplification of
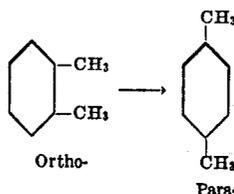the problem but is illustrative of its nature.

Without reference to the mechanism of the
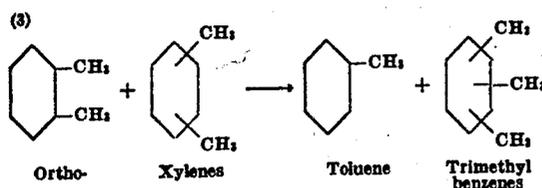reactions the main conversions for orthoxylene
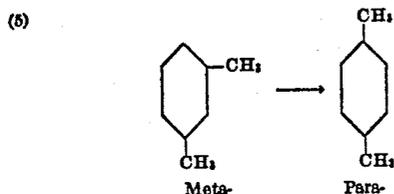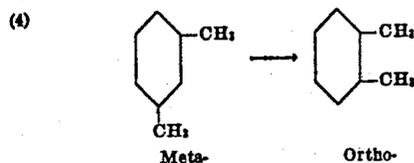may be written:

(1) Ortho- → Meta-

(2) Ortho- → Para-
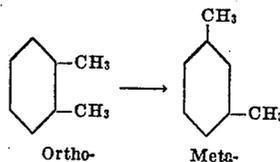
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Orthoxylene also tends to enter side reactions, such as disproportionation:

(3)

Ortho-   Xylenes   Toluene   Trimethyl benzenes

Upon isomerization meta xylene may be correspondingly converted:

(4)

Meta-   Ortho-

(5)

Meta-   Para-

Likewise, metal xylene tends to enter side reactions illustrated by:

(6)

Meta-   Xylenes   Toluene   Trimethyl benzenes
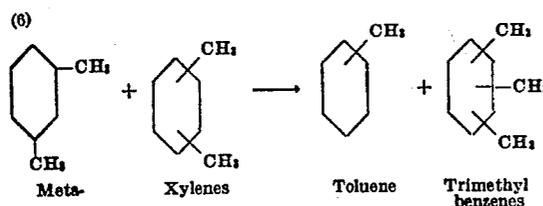
Para xylene isomers react analogously:

(7)

Para   Meta

(8)

Para   Ortho
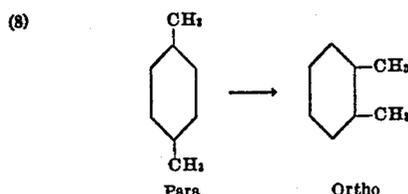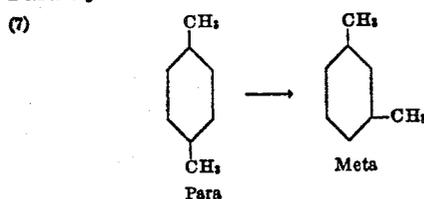
Again there are side reactions:

(9)

Para   Xylenes   Trimethi benzene   Toluene
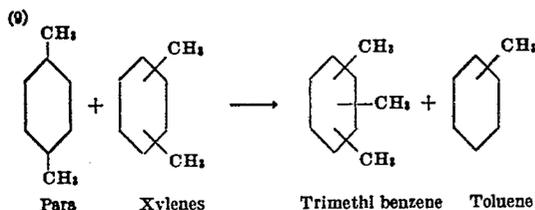
Of course, each of the foregoing reaction products may further react with the xylene and with each other to introduce additional complications.

This invention involves catalysis of the foregoing desired isomerization reactions with hydrogen fluoride. The catalytic action of hydrogen fluoride in isomerizations of this type is re-

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markable because it can be made highly selective for the desired shifting of substituents at the ring. Thus, the isomerization of xylenes by hydrogen fluoride catalysis may be effected with a minimum of side reactions such as disproportionation and formation of trimethylbenzene or toluene. The catalytic action of hydrogen fluoride also lowers the temperature at which isomerization at the ring will occur and thereby reduces or avoids undesirable losses by dealkylation, cracking and other reactions heretofore encountered in various high temperature thermal processes.

Hydrogen fluoride catalysis in conformance with this invention and discovery provides a valuable process for converting ortho xylene to a mixture of meta and para xylene isomers or for producing ortho and para isomers from meta xylene or for obtaining ortho and meta xylenes from the para isomer. In effecting these reactions, it has been found that isomerization is an equilibrium reaction, and the proportions of xylene isomers at equilibrium is about the same at any given temperature irrespective of the particular isomer or mixture undergoing conversion. These relative proportions in the present process ordinarily are approximately:

	Per cent
Orthoxylene	19
Paraxylene	21
Metaxylene	60

However, it has been found that isomerization of meta xylene to ortho or para xylenes, as well as conversion of either para or ortho xylene to the meta product are first order reactions with respect to the xylene being isomerized and that the specific reaction rate constant for conversion of meta to para is about twice that for the conversion of meta to ortho xylene. On the other hand conversion of ortho to para xylene has been found to occur in a stepwise fashion through the meta isomer. These discoveries make is possible to stop the reaction short of equilibrium and effect the following conversions selectively:

> Meta→para
> Para→meta
> Ortho→meta

while substantially inhibiting though not avoiding the reactions:

> Ortho→para
> Para→ortho
> Meta→ortho

Such selectivity may be obtained by shortening the reaction period sufficiently to utilize the differential reaction rates, for example, stopping the reaction by quenching to a temperature below about 200 to 250° F. prior to formation of about 60% of the equilibrium proportion of ortho xylene. The foregoing selective reactions may be further promoted by the presence of the undesired isomer in the reaction mixture. Thus:

> Meta→para (in the presence of ortho)
> Para→meta (in the presence of ortho)
> Ortho→meta (in the presence of para)

In practicing this invention it is preferred to feed a mixture of xylenes containing at least one isomer in a proportion different from that represented by isomerization equilibrium or formed by the isomerization reaction. This gives a conversion corresponding to the difference in composition of feed and reaction product, which can be relatively large as desired. Conversion or isom-

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erization by such differentials has the advantage of avoiding difficult and expensive purification treatments otherwise necessary to supply a feed stock of any given pure isomer. On the other hand, such differential conversion processes necessitate adequate suppression of side reactions and involve problems of build-up of impurities such as ethyl benzene.

The reaction product in the preferred isomerization by differential conversion will contain all three isomeric xylenes. In addition to accepting reduced conversions, it is preferred and usually necessary to accept considerably less than 100 per cent recovery of the desired isomer or isomers from any single pass isomerization product. Nevertheless high overall conversions and yields can be obtained by removing a substantial proportion of the desired isomer from the reaction product and again subjecting the remaining isomers to isomerization to replace the isomer which has been withdrawn. Repeated removal of desired isomer followed by repeated recycle of residual reaction products to the isomerization zone ultimately affords substantially complete conversion of any xylene mixture to the selected isomer or mixture of isomers. However, it will be apparent from the foregoing that the amount of side reactions becomes of critical importance in such a cyclic process.

In the production of para xylene, for example, a maximum of about 10% of the xylenes in the reaction product is removable by crystallization which in turn signifies that only about 10% conversion per pass can be obtained upon recycle through the isomerization zone. For 100% overall conversion of a xylene fraction to paraxylene about 10 passes are therefore required. It follows that if only 5% of the xylenes are converted to side reaction products, each time the reaction is effected, the real loss in xylenes is not 5% but 33% in such a cyclic process. When it is recalled that, generally, a single pass or batch organic preparation would be considered excellent if only 5% loss to side reactions took place, it is evident that ordinarily highly acceptable standards for organic reactions are likely to introduce economically prohibitive losses in the isomerization of this invention.

In accordance with this invention xylenes are isomerized at the benzene ring by a new and improved differential conversion process which is capable of converting either a single xylene isomer or a mixture of xylenes substantially entirely to any selected xylene isomer or mixture, economically and with minimized loss to side reaction products or production of disproportionation products. Ethyl benzene impurity is eliminated simultaneously by disproportionation. Suitable reaction conditions will be apparent from the following discussion of process variables particularly applicable to the xylenes:

A temperature of above about 250° F. is operative, the upper operative temperature limit for isomerization being primarily determined by permissible pressures. Generally temperatures higher than 400° F. are not warranted and tend to introduce or increase side reactions. It is to be understood that less severe conditions, i. e., lower temperatures or lower contact times, or both, are acceptable, and even preferable, for isomerization of ethyl and higher molecular weight aliphatic side chains. Ethyl groups are much more easily isomerized at the aromatic nucleus than are methyl groups, for example, and temperatures below 250° F. will be found suitable

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for such higher alkyl chains. In the case of isomerization of methyl groups at the nucleus, 300–375° F. is desirable and a temperature of from about 310–350° F. has been found preferable for the isomerization of xylenes with anhydrous hydrogen fluoride. These higher temperatures also are preferred for xylenes containing ethyl benzene impurities to remove this component simultaneously by disproportionation.

Contact time for a given conversion in the isomerization reaction is a function of temperature, catalyst concentration and feed concentration. Ordinarily, a minimum of about one minute will be required and the maximum contact time is primarily determined by permissible plant size, although the danger of increasing relatively slow side reactions is increased by inordinately long contacts. Generally thirty minutes is a maximum, and five to twenty minutes is presently regarded as optimum for isomerization of xylenes with anhydrous hydrogen fluoride in the proportions and at the temperatures herein recommended.

Catalyst concentration in the reaction mixture may be varied widely. Although not critical to operativeness of the isomerization reactions, it has been discovered that by adjusting reaction conditions remarkable and unpredictable improvements may be obtained and that the isomerization may be effected as a homogeneous liquid phase reaction. To effect such a homogeneous reaction rapidly, relatively high proportions of hydrogen fluoride are utilized, for example, from about 60 to about 85 volume per cent of anhydrous hydrogen fluoride based on the total reaction mixture. Smaller amounts are operable, but at least 40 per cent by volume is desirable for xylene isomerization, depending upon temperature and pressure. The maximum proportion of catalyst is determined primarily by acceptable plant size, but more than 90 per cent by volume based on total reaction mixture ordinarily is not warranted.

Commercial anhydrous hydrogen fluoride may contain up to about 0.5% water and such anhydrous hydrogen fluoride is preferred as a catalyst, although small amounts of water, for example, 2 to 5% are not precluded. Water in the hydrogen fluoride catalyst reduces the activity of the catalyst by decreasing the mol fraction of hydrogen fluoride, and consequently reduces either the reaction rate, or the capacity of the system for hydrocarbon if the amount of aqueous catalyst is increased to yield an equivalent HF mol fraction. An additional loss of 35% in activity was found for hydrogen fluoride containing 2 to 4% water when compared to anhydrous hydrogen fluoride at equivalent mol fractions of HF. This may be compensated for by raising the temperature of operation. The invention embraces processes in which hydrogen fluoride is the effective catalyst and does not preclude the presence of auxiliary catalytic agents. The term "the effective catalyst" used in the claims with reference to hydrogen fluoride is intended to mean that hydrogen fluoride is present in an amount and concentration sufficient to act as the sole catalyst necessary to carry out the reaction. This terminology is intended to cover not only isomerizations at the aromatic nucleus where hydrogen fluoride is the only catalytic agent present, but also such isomerization reactions where, in addition to hydrogen fluoride, other catalytic materials are added in amounts such that in the ab-

sence of hydrogen fluoride satisfactory catalysis of the reaction would not be effected.

The presence of a hydrocarbon diluent miscible with the reaction mixture selectively promotes the isomerization reaction, that is, the same fractional conversions of meta or ortho xylene to para xylene, for example, are obtained in diluted solutions as in more concentrated ones under otherwise comparable conditions. By contrast second order reactions, such as disproportionation, are selectively reduced or inhibited by dilution of the reaction mixture. Additionally, it has been found that by using toluene as a diluent, losses by disproportionation of xylenes are reduced over and above the reduction obtained with substantially inert diluents, such as cyclohexane. For these reasons, it is preferred to effect the isomerization reaction in the presence of a diluent, most desirably toluene with xylene isomerization; and for other dialkyl benzenes, the preferred diluent is a mono-alkyl benzene in which the alkyl group is like an alkyl group of the dialkyl benzene being isomerized. Suitable proportions of diluent usually are in excess of 10% and desirably in the order of 50% by volume based on the total feed.

Pressure is not critical except that it should be sufficiently high to maintain reactants and catalyst in liquid phase. In order to maintain catalyst activity or at least to keep its reduction to a controlled minimum, the hydrocarbon feed and diluent desirably should be dried prior to contacting with the hydrogen fluoride catalyst. Any suitable drying process may be adopted, for example, contacting with bauxite or other porous adsorbents for water.

The principal impurities in xylene fractions here contemplated are of two types: (a) aromatic hydrocarbons boiling in the same range as the xylenes or forming constant boiling mixtures therewith; (b) unsulfonatable hydrocarbons normally designated paraffinic and likewise boiling in the same range or forming constant boiling mixtures with the xylenes. In a cyclic differential isomerization process, such impurities must be dealt with even though present only in minor proportions in the feed, since repeated recycling of the isomerized fraction (with removal of the desired isomer only) allows and causes a buildup in the concentration of such impurities. In the present process the ethyl benzene impurity is disproportionated selectively during the isomerization reaction and converted to benzene with formation of ethyl toluene and ethyl xylenes, each of which can be eliminated readily by simple fractional distillation. Inordinate increase in ethyl benzene concentration is thus prevented in the presently preferred cyclic process for differentially isomerizing mixed xylenes. Paraffinic impurities on the other hand desirably are eliminated if present. Various methods are feasible such as selective solvent extraction and azeotropic distillation, but the so-called solvent distillation or perhaps more accurately designated "extractive distillation" is presently preferred.

In the drawing, Fig. 1 is a schematic flow sheet of a process and apparatus illustrating only the major unit operations in the combination process of this invention;

Fig. 2 is a more detailed flow sheet of the isomerization stage of a process and apparatus for xylene conversion;

Fig. 3 illustrates a combination of isomerization and separation stages adapted to produce xylene isomers in any desired relative proportion;

Figs. 4 and 5 illustrate the effects of proportion of hydrogen fluoride catalyst on specific rate constants for isomerization and disproportionation.

For purposes of simplicity and to avoid incorporation of unnecessary details of Fig. 2, the isomerization unit of Figs. 1 and 3 is shown in block diagram.

Referring to Fig. 1, polyalkyl benzene feed is introduced into the system by inlet line 10, and for purposes of simplicity the process will be illustrated with reference to a xylene feed. Examples of suitable xylene feeds are meta xylene, para xylene, mixtures of meta and para xylene or mixtures of meta, para and ortho xylenes in which the desired isomer is present in less than the relative proportion formed upon completion of the isomerization reaction. In the production of para xylene, for example, the feed should contain less than 14% para xylene based on the xylene content of the feed. In the preferred process, about 10% or less of the xylene isomers in the feed is para xylene. The xylene feed ordinarily contains impurities principally paraffins and ethyl benzene.

As here shown an extractive distillation is utilized to effect removal of paraffins contained in the feed. Details of a suitable process are exemplified in U. S. Patent No. 2,215,915 to Cope et al. issued September 24, 1940. In accordance with this process, the xylene passes by way of xylene inlet line 10 through heater 11 to extractive distillation column 12 where the downwardly flowing selective solvent, introduced in the top of the column by solvent line 13, serves to carry the extracted xylenes downwardly in liquid phase. Heater coil 14 boils paraffinic components of the mixture out of the liquid phase solvent, and these boiling vapors are repeatedly fractionated and contacted with selective solvent to separate any xylenes as the vapors progress upwardly through the distillation column 12. A suitable condenser and reflux is provided in paraffin discharge line 16 at the top of column 12, and the discharged paraffins pass through line 17 to storage.

Liquid phase solvent together with dissolved xylenes and ethyl benzene or other aromatic impurities present in the original xylene fraction flow from the bottom of column 12 through discharge line 18 to fractionator 19 where the dissolved aromatics are separated from the higher boiling selective solvent by conventional fractionation procedure. The solvent is recycled from the bottom of this fractionator by way of discharge conduit 21 to extractive distillation column 12. Aromatic hydrocarbons vaporized in fractionator 19 flow by outlet line 22 through condenser 23 to reflux drum 24, from which a portion may be returned by way of valve-controlled reflux line 26 to fractionator 19 for purposes of improving separation of the selective solvent from the xylene fraction, when and if they boil sufficiently close to warrant such an expedient. The main portion of the purified xylene from reflux drum 24 passes through valve-controlled header 27 to the isomerization stage 28.

The presently preferred form of isomerization unit is illustrated in Fig. 2 later to be described. However, the invention in its broader aspects is not limited to the particular isomerization stage there shown, since features for selectively promoting isomerization while suppressing disproportionation of the desired polyalkyl benzenes are applicable to other types of isomerization units, where hydrofluoric acid catalysis is utilized

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for conversion of a polyalkyl aromatic compound to an isomer.

In order to favor the isomerization reaction while selectively reducing or inhibiting side reactions, such as disproportionation, a diluent is added to the isomerization feed in header 27 by way of valve-controlled diluent inlet 29. When the polyalkyl aromatic feed is xylene, the preferred diluent is toluene as previously disclosed. Despite the diluent, ethyl benzene is disproportionated while xylenes are isomerized. Catalyst is supplied to the isomerization stage through valve-controlled line 31 as shown.

The isomerized hydrocarbon mixture stripped of catalyst flows from the isomerization unit through product discharge line 32 to diluent fractionator 33 where the desirably more volatile diluent is distilled as overhead and returned through diluent recycle line 34 to isomerization feed header 27. Fractionator 33 is provided with a condenser 36 and condensate drum 37 in order that a portion of the diluent may be returned as reflux through valve-controlled line 38 or withdrawn when desired by means of valve-controlled line 39.

Isomerized hydrocarbons stripped of diluent flow from the bottom of fractionator 33 by way of line 40 to a purification unit 41 comprising a fractionating column provided with an overhead condenser 42 and condensate drum 43. The desired isomerizates are distilled overhead in fractionator 41, a portion thereof being refluxed through valve-controlled line 44, and the remainder passed through valve-controlled line 46 to isomer separation stage 47. Bottoms from fractionator 41 comprise principally higher boiling disproportionation products of ethyl benzene such as ethyl toluene and ethyl xylenes, when the isomerization feed is xylenes diluted with toluene. Also, some trimethyl benzenes are formed from the xylenes. To further favor the isomerization reaction, reduce loss of xylenes by side reactions and suppress formation of disproportionation products from the xylenes, it has been found that these heavier impurities should be recycled at least in part to the isomerization feed as shown by valve-controlled heavy recycle line 48. Further, to facilitate and expedite control of the isomerization reaction in relation to side reactions, the heavier recycle fraction may be separated, for example, into a C9 and C10 fraction by conveying at least part thereof through valve-controlled line 49 to fractionating column 51, where C9 alkyl benzenes are taken overhead and C10 removed as bottoms, whereupon the relative proportions of C9 and C10 recycle can be altered and controlled to give optimum suppression of side reactions. Thus, one may wish to remove from the system primarily those disproportionation products containing an ethyl group (for example, ethyl toluene or ethyl xylene or both) while recycling primarily trimethyl benzenes. Independent recycle lines 52 and 53 are provided for this purpose.

Returning now to the separation of isomers in the stage 47, the desired isomeric product is removed by way of line 54, and the remaining isomers preferably are returned to the isomerization stage by way of recycle line 56. The return of these remaining isomers serve to promote the production of the desired isomer. Thus, recycle of ortho and meta xylenes, for example, suppresses further formation of these components during isomerization and promotes the conversion of xylenes in the feed to the para isomer. By

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recycling all ortho and meta xylenes, the entire isomerization thus can be devoted to the production of the para product. Likewise, the ortho or the meta isomer may be selected as a desired product and the corresponding remaining isomers recycled.

The precise separation procedure utilized in stage 47 will depend upon the isomer or isomers to be obtained as a final product. In the production of para xylene, for example, ortho xylene, meta xylene, a mixture of ortho and meta, or a mixture of xylenes containing a smaller proportion of para than is present in the isomerized reaction product, will be fed to the isomerization stage. Separation of para xylene product in stage 47 desirably is effected by selective crystallization, although other methods may be utilized, such as selective sulfonation of the meta xylene isomer, separation of an unsulfonated oil layer from the sulfonation reaction mixture and fractional distillation of the para from the ortho xylenes in the unsulfonated oil. Crystallization of para xylene is effected, for example, by chilling the xylene mixture to a temperature of from at least about —50° F. and preferably to about —65° F. with separation of the crystals while so chilled. When the isomeric xylene fraction is free of other hydrocarbon contaminants, temperatures below —67° F. serve to introduce other isomeric xylenes as impurities in the crystallized para xylene fraction. For additional purification the separated para xylene crystals may be washed with a suitable solvent, such as isopentane and/or melted and subjected to a second crystallization operation.

Ortho xylene can be produced in separation stage 47 by close distillation preferably by superfractionation to yield an ortho xylene product of 95% and higher purity as a bottom fraction. However, for some purposes, a 70–90% or more desirably a 85–95% ortho xylene rich product is acceptable. The ortho xylene poor overhead from the superfractionation will then be recycled to the isomerization stage when and if the only desired isomer is the ortho product.

Production of meta xylene as the desired isomer requires a different separation in stage 47 and the presently preferred method for recovering meta xylene product involves selective sulfonation of the isomerization reaction product to selectively form a meta xylene sulfonic acid phase and a supernatant oil layer containing predominantly ortho and para xylenes. These phases are separated by any suitable method, and the meta xylene sulfonic acid layer is converted back to meta xylene by hydrolysis. The meta xylene desirably is removed from the hydrolysis reaction zone by distillation, and residual sulfonic acids may be hydrolyzed to recover any ortho and para xylenes carried thereby. Suitable conditions for separation and recovery of meta xylene by selective sulfonation and selective hydrolysis are illustrated by the following.

It is preferred to use about two mols of sulfuric acid (96–98%) for each mol of meta xylene in the mixture being treated, although these proportions are not critical. Weaker acid may be utilized down to about 75%, though more acid and higher temperature, or greater time, or both, are required. The temperature of selective sulfonation ranges from about 80° F. to about 180° F. with a corresponding variation in the rate of sulfonation. The selective hydrolysis preferably is carried out by first heating the separated sulfonic acid mixture up to a temperature such that hy-

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drocarbon vapors distill off and until the temperature reaches about 250° F. This initial distillate is condensed and comprises a para xylene rich fraction which may be utilized as such or recycled to isomerization. The second stage of the hydrolysis is effected by heating the resulting sulfonic acid solution in the presence of water or steam at a temperature of from about 250–300° F. Meta xylene vapors are thus selectively distilled off from the reaction mixture at these temperatures to yield fractions of 90% and higher purity. Residual hydrocarbon sulfonic acids remaining in the still bottoms are finally hydrolyzed by raising the temperature of the reaction mixture to about 360–460° F., collecting and condensing hydrocarbon vapors therefrom to form a second para rich xylene fraction which desirably is recycled to isomerization.

Provision has been made for removal of paraffinic impurities in two stages for those cases where complete elimination of these impurities in the feed is difficult or unduly expensive. In this two-stage operation a major portion of the paraffins is eliminated from the feed as previously described. In a cyclic operation paraffins eventually may build up; however, by reason of continued return of small quantities of paraffins from the isomer separation to the isomerization stage, this build-up is controlled by a second stage separation effected as here shown by diverting at least a portion of the recycle stock from recycle line 56 by way of a purification return line 57 through heat exchanger 58 to extractive distillation column 12. Thus, paraffin build-up can be eliminated entirely or controlled to a given level by regulating the proportion or frequency of diversion of recycle xylenes to extractive distillation column 12.

As previously noted, ethyl benzene build-up is prevented by disproportionation to form either ethyl toluene or ethyl xylene, or both, as desired. Build-up of disproportionation product or products of ethyl benzene may be controlled by diverting a portion of selected heavy recycle streams. Thus, C₉ disproportionation products may be removed from overhead distillate in fractionator 51 by withdrawal through valve-controlled line 59 and disproportionation of the ethyl benzene to ethyl xylene suppressed by recycling C₁₀ disproportionation products to isomerization stage through line 52. However, it may be found desirable to remove a portion of these heavier products by way of valve-controlled line 61 while recycling both the C₉ and heavier disproportionation products to isomerization.

The preferred isomerization system of Fig. 2 likewise will be illustrated and described in connection with the isomerization of xylenes. Xylene feed from header 27 is diluted with toluene introduced through valve-controlled line 29 and the mixture flows through heater 66 and mixer 67 to isomerization reactor 68. Hydrogen fluoride catalyst is supplied from storage and passes from valve-controlled inlet 69 through heater 71 and is blended with the hydrocarbon feed in mixer 67.

A single phase homogeneous reaction mixture can be formed with hydrogen fluoride catalyst by mixing and blending under suitable conditions. The preferred expedient for production of a single phase is maintenance of temperature above the point of miscibility of hydrocarbon with hydrogen fluoride while retaining sufficient pressure to retain the hydrogen fluoride catalyst in liquid phase. Desirably, relatively large proportions of hydro-

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gen fluoride catalyst are utilized, for example, at least 40% by volume of the entire reaction mixture and more desirably 60–80% by volume. Ratios as high as ten parts anhydrous hydrogen fluoride to one part of hydrocarbon in the reaction mixture may be utilized; and in general, solutions are preferred in which hydrogen fluoride is the major component and hydrocarbons fed to the reaction zone are minor components. The blended single phase solution formed in mixer 67 is maintained as such throughout isomerization reaction zone 68.

Although the isomerization process is operative where agitation is effected in the reaction zone, the process is effected more efficiently and the reaction rate is increased by utilizing an agitated blending zone of relatively small volume in combination with a quiescent reaction zone, where homogeneous liquid phase conditions are maintained for a relatively long residence time as compared with the mixing or blending zone. Thus, in the preferred isomerization process hydrocarbon feed and hydrogen fluoride catalyst are continuously passed through the relatively small mixer 67 into relatively large single phase liquid reaction zone 68, where a differential in hydrocarbon composition is maintained through the reaction zone from inlet to outlet by preventing substantial dilution of reaction mixture at the inlet with reaction mixture or hydrocarbons from the outlet of the reaction zone. This feature of maintaining a differential in hydrocarbon composition despite the fact that only a single liquid phase reaction mixture is utilized yields several advantages and new results including: Reduction of loss from relatively slow side reactions and increase in the overall conversion rate in the reaction zone, and elimination of hazards attending operation of agitators in large volume of hydrogen fluoride reactor vessels inherent in possible failure of agitator bearings and sealing devices.

In reactor 68, the single phase hydrogen fluoride-hydrocarbon mixture is maintained at temperatures above 250° F. and under sufficient pressure to insure liquid phase operation. The rate of flow through the reactor is controlled so that turbulence is kept at a minimum and prevention of mixing of inlet feed with outlet isomerizate is assured by baffle plates 72.

In order to effect initial separation of hydrogen fluoride catalyst and hydrocarbon isomerizate, the reaction mixture is withdrawn through outlet conduit 73 and cooled by heat exchanger 74 to a temperature substantially below that of complete miscibility, for example, 70° F., whereupon a hydrocarbon phase saturated with hydrogen fluoride catalyst and a hydrogen fluoride catalyst phase saturated with hydrocarbon are formed. This two-phase system is separated in settler 76 and the upper oil phase withdrawn to outlet 77 and passed to the hydrocarbon recovery system. The hydrogen fluoride catalyst phase passes from the bottom of settler 76 through outlet 78 and is recycled through valve-controlled hydrogen fluoride return line 79 to heater 71 and mixer 67 where it is blended with incoming hydrocarbon feed as previously described.

The first stage of the recovery system for hydrocarbon isomerizate is a hydrogen fluoride stripper 81 in which hydrogen fluoride is fractionated and removed as overhead through outlet line 82, condenser 83 to reflux drum 84. A portion of the hydrogen fluoride overhead may be recycled to the stripping column 81 by means

of valve-controlled reflux line **86** and the remainder passes by way of line **87** to catalyst recycle. Hydrocarbon isomerizate stripped of hydrogen fluoride flows from the bottom of stripper **81** by way of outlet line **88** to fractionator **89** where hydrocarbons boiling below the xylenes are removed as overhead. These lower boiling hydrocarbons, comprising principally toluene diluent with some benzene which may be formed during the isomerization reaction flow as overhead through outlet **91**, condenser **92** to condensate drum **93**. A portion of the condensate is refluxed to column **89** by way of valve-controlled line **94**, and the remainder is passed through valve-controlled line **95** and may be returned directly to feed through valve-controlled line **96** to serve as a reaction diluent or through valve-controlled line **97** to benzene still **98**. In the latter instance the benzene and toluene are separated, benzene being removed as overhead to storage through the usual reflux system. Toluene is taken as fractionator bottoms and recycled via line **99** to xylene feed conduit **27**.

Xylene and heavier hydrocarbon fractions flow from the bottom of fractionating column **89** by way of conduit **101** to fractionating column **102** for the distillation of xylene from higher boiling reaction products. The isomerized xylenes pass as overhead through outlet conduit **103**, condenser **104** and reflux drum **105** to xylene isomer separation unit **47** by way of isomerizate outlet line **106**. A portion of the xylenes is returned as reflux from drum **105** through valve-controlled line **107** to improved fractionation in column **102**.

C₉ and heavier alkyl aromatic hydrocarbons formed during the isomerization are withdrawn from the bottom of fractionator **102**. These fractions may be recycled in total by way of valve-controlled line **108**, or more desirably at least a portion thereof removed by way of valve-controlled line **109** for a separation of C₉ and C₁₀ alkyl aromatics and controlled recycle to xylene feed line **27** of the C₉ and C₁₀ fractions as previously described.

Water in the hydrogen fluoride catalyst decreases the catalyst activity and the mol fraction of hydrogen fluoride in the catalyst. It is therefore desirable to dehydrate all feed stocks entering the isomerization system. Even with the most efficient dehydration methods, the hydrogen fluoride catalyst tends to pick up water from the hydrocarbon feed or other sources. Provision is made for maintaining hydrogen fluoride in the desired concentration and for removal of water as an aqueous hydrogen fluoride solution by distillation. As here shown, valve-controlled line **110** serves for withdrawal of hydrogen fluoride catalyst from settler outlet line **78**. The withdrawn hydrogen fluoride passes to fractionating column **111** where substantially anhydrous hydrogen fluoride may be taken off as overhead through outlet conduit **112**, cooler **113** to reflux drum **114**. The purified hydrogen fluoride then passes by way of valve-controlled line **116** to catalyst return **79**. Suitable reflux is provided through valve-controlled conduit **117**. A constant boiling mixture of hydrogen fluoride and water is withdrawn, together with a contaminating oil, from the bottom of fractionator **111** through outlet conduit **118**.

A flexible and versatile process for isomerization of xylenes is illustrated in the flow sheet of Fig. 3. In this process there is provided an isomerization zone **120** from which the reaction

product may flow through outlet header **121** to an ortho xylene recovery unit including fractionating columns **122** and **123**, a meta xylene recovery unit and a para xylene recovery unit **128**. The meta xylene recovery stage comprises selective sulfonation and selective hydrolysis units **124**, **126** and **127**, and as here shown the para xylene is recovered in selective crystallization stage **128**. The operation of this combination process can be adapted to treatment of any xylene mixture for the production of any one or more of the desired isomers in any relative proportions which may be specified. The types of operations may be classified in accordance with the feed stock available as follows:

Case I.—Feed is mixture of ortho, meta and para xylene in proportions substantially equal to the equilibrium isomerization mixture.

Case II.—Feed is a xylene fraction containing more ortho xylene than in the equilibrium mixture.

Case III.—Feed is a xylene fraction containing more para xylene than in the equilibrium mixture.

Case IV.—Feed is a xylene fraction containing more meta xylene than in the equilibrium mixture.

These feeds may be two or three xylene component mixtures. When the three xylenes are present, the two minor components may be present in an equilibrium ratio (with respect to each other) or in a ratio other than equilibrium.

In each of the foregoing major cases, it may be desired to operate the process to yield:

(a) Primarily ortho xylene and apportioned meta and para xylenes;

(b) Primarily meta xylene and apportioned ortho and para xylenes;

(c) Primarily para xylene and apportioned ortho and meta xylenes.

In the production of xylenes as in Case I, when the process of Fig. 3 is operated to yield primarily ortho xylene, the xylene feed admitted by way of inlet header **129** passes through valve-controlled line **131** to fractionating column **122** of the ortho xylene recovery unit by way of fractionator inlet **132**. Meta and para xylene are distilled overhead and ortho xylene flows as a bottoms fraction by way of line **133** to still **123**. Any C₉ heavier hydrocarbons present are removed in this latter still and the ortho xylene is passed by way of outlet **136** to storage.

The meta and para rich overhead from ortho xylene fractionating column **122** flows to hydrogen fluoride isomerization unit **120** by way of valve-controlled line **137**. Hydrofluoric acid catalyst is admitted to the isomerization zone and recovered from the isomerized hydrocarbons as previously disclosed in connection with the specific description of Fig. 2. Hydrocarbon isomerizate passes through outlet **121** and is again recycled to ortho xylene recovery column **122**. A selected portion of the meta-para rich xylene fraction from ortho xylene fractionator **122** is diverted by way of valve-controlled line **138** to meta and para recovery units.

As here shown, this diverted meta-para rich fraction is apportioned between the para xylene and the meta xylene recovery units by way of valve-controlled lines **139** and **141** respectively. Thus, a portion of flows from line **139** to selective crystallization unit **128** by way of inlet header **142**, and a second portion flows from

line 141 to selective sulfonation unit 124 by way of inlet 143.

A para xylene fraction is removed by selective crystallization in unit 128 and passes to storage through outlet 144. The remaining mother liquor flows by way of recycle outlet 146 to any of three destinations as desired. First, it may be returned to valve-controlled line 147 through ortho xylene recycle header 148 to inlet 132 of the ortho xylene recovery unit. Secondly, when the production of meta xylene is to be increased, crystallization mother liquor is passed through meta xylene recycle line 149 to inlet 143 of the meta xylene recovery system. Finally, crystallization mother liquor may flow by way of valve-controlled conduit 151 through isomerization recycle line 152 to isomerization unit 120.

In the meta xylene recovery unit the meta-para rich feed admitted by way of inlet 143 is selectively sulfonated in reactor 124 and the reaction mixture allowed to settle into an upper unsulfonated oil phase and a lower meta xylene sulfonic acid phase. The sulfonic acid phase passes through line 153 to selective hydrolysis unit 126 where entrained or loosely held ortho and para xylenes are initially distilled off. The meta xylene sulfonic acids are then selectively hydrolyzed and meta xylene removed by steam distillation. Meta xylene so recovered is passed through outlet line 154 to storage. Frequently xylene sulfonic acid impurities rich in para xylene remain in the acid layer and additional xylenes may be recovered by hydrolysis in final stage 127 to free a para-rich fraction. This para-rich fraction is removed through line 156 and may be blended with unsulfonated meta and para xylenes from selective sulfonation stage 124. These two xylene fractions are passed to header 157 and may flow to any one of three destinations as desired. Thus, the para-rich xylene fraction from selective sulfonation may be returned from header 157 through valve-controlled line 148 to ortho xylene recovery fractionator 122 by way of inlet 132. But more usually the ortho xylene content of the para-rich fraction will not be sufficiently large to justify this procedure and the para-rich fraction more desirably flows from header 157 by way of recycle line 158 to inlet 142 of para xylene crystallization unit 128. However, if the demand for para xylene does not warrent this recovery, the para-rich fraction may alternately be passed through header 157 by way of valve-controlled line 159 and isomerization recycle line 152 to isomerization unit 120.

The foregoing description concerning the operation of the process of Fig. 3 has been with respect to Case I (a), that is, feeding an equilibrium mixture of xylenes to recover primarily otho xylene and apportioned meta and para xylenes. If para xylene recovery is the primary object, the feed may be passed directly from inlet 129 through valve-controlled conduit 161 to selective crystallization unit 128, para xylene crystals removed, and the mother liquor apportioned between isomerization recycle and the ortho and meta xylene recovery units respectively. Likewise, if meta xylene is the primary product, the feed may flow directly to selective sulfonation unit 124 by way of valve-controlled line 162, and the unsulfonated oil layer apportioned between recycle to isomerization and ortho and para recovery units. Again, when the feed to the system contains more ortho xylene than in the equilibrium mixture (Case II), more

para xylene than in the equilibrium mixture (Case III), or more meta xylene than in the equilibrium mixture (Case IV), these respective feeds will be passed, first, to the isomerization unit unless the particular isomer desired as a primary product is the same as that contained in excess in the feed. In the latter event the feed will pass first to the recovery unit for the isomer present in excess.

In order to guide those skilled in the art in the practice of the invention and to illustrate the directional effect of various significant variables in the process, illustrative data are given in the following examples and in the graphs of Figs. 4 and 5. The term "raffinate" as used throughout the specification and claims denotes the hydrocarbon phase separated from the hydrogen fluoride acid phase after removal from the isomerization reaction zone. This raffinate of the subject reaction product contains substantially the whole of the isomerization product and is exclusive of the acid phase which contains the hydrogen fluoride catalyst together with small amounts of catalyst complex.

EXAMPLE 1

Isomerization was effected in a batch reactor without stirring at a reaction temperature maintained within the range of from 300–385° F. and a contact time of 15–20 minutes. Maximum pressure was 1,040 pounds gauge and the weight ratio of xylene to anhydrous hydrogen fluoride catalyst was 0.3. Volume ratio of toluene diluent to xylene was 1:1. Following is a tabulation of approximate composition of feed and raffinate:

	Feed	Raffinate
Toluene	50.1	50.0
Ethyl benzene	0.3	1.0
Ortho xylene	0.3	5.2
Meta xylene	48.8	33.9
Para xylene	0.5	9.1
Bottoms	0.0	0.8

The xylene fraction recovered from the reaction mixture contains 10.8% ortho xylene, 70.4% meta xylene and 18.8% para xylene. Approximately 90% of maximum para xylene was thus produced and only a very small percentage of the xylenes was disproportionated. The foregoing compositions are given in volume per cent.

EXAMPLE 2

Isomerization was effected in a batch reactor without stirring at a reaction temperature maintained within the range of from 300–332° F. and a contact time of seven minutes. Maximum pressure was 560 pounds gauge, and the weight ratio of xylene to anhydrous hydrogen fluoride catalyst was 0.3. Volume ratio of toluene diluent to xylene was 1:1. Following is a tabulation of approximate composition of feed and raffinate:

	Feed	Raffinate
Toluene	50.1	48.6
Ethyl benzene	0.3	0.9
Ortho xylene	0.3	3.5
Meta xylene	48.8	39.6
Para xylene	0.5	7.1
Bottoms	0.0	0.3

The composition of the xylene fraction recovered from the reaction mixture contains 7.0% ortho xylene, 78.8% meta xylene and 14.2% para

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xylene. Approximately 68% of maximum para xylene was produced and only a very small percentage of the xylenes was disproportionated. The foregoing compositions are given in volume per cent.

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Xylenes were isomerized in a continuous process utilizing a tubular reactor for the provision of a quiescent or unagitated reaction zone. Tables I, II, and III give exemplary data under various reaction conditions.

TABLE I

Isomerization of xylenes by HF-tubular reactor

Example No.	3 Feed	3 Prod	4 Feed	4 Prod	5 Feed	5 Prod	6 Feed	6 Prod
Operating Conditions:								
Temperature, °F	309		309		309		309	
Contact Time, Min	19.6		14.0		10.2		10.9	
Vol. Per Cent HF in Reactor	55		66		80		73	
Diluent	None		None		None		Toluene	
Vol. Per Cent Diluent in Feed							50	
"Raffinate" Phase, Grams	897		911		551		2,755	
HF Extract:								
Grams	16.2		28		30.3		67	
Bromine No.	7		3		3		2	
Compositions, Vol. Per Cent:								
Benzene								
Toluene	0.4_2	2.8_6	0.4_3	2.4_4	0.4_3	2.7_7	50.0	49.6
Ethylbenzene		0.0		0.0		0.0		0.0
Ortho Xylene		9.0		11.1		12.4		6.1
Meta Xylene	97.1	72.5	97.1	67.8	97.1	62.7	48.6	33.8
Para Xylene		12.4		15.9		18.8		9.5
Bottoms	0.38	3.1_6	0.3_8	2.7_7	0.3_8	3.2_6	0.1_9	1.0_2
Xylene Fraction, Vol. Per Cent:								
Ortho		9.6		11.7		13.2		12.4
Meta		77.2		71.5		66.8		68.3
Para		13.2		16.8		20.0		19.3
Per Cent of Max. Para Xylene Produced	63		80					
Per Cent Xylenes Disproportionated						95		92
Specific Rate Constant, $m{\to}p$, k_1	.012		.026		.049		.040	
Specific Rate Constant, Disproportionation, k_2	.00158		.00171		.00334		.00302	

NOTE.—Figures appearing as subscripts in the above table are observed analytical values of doubtful accuracy.

TABLE II

Isomerization of xylenes by HF-tubular reactor

Example No.	7 Feed	7 Prod	8 Feed	8 Prod	9 Feed	9 Prod	10 Feed	10 Prod	11 Feed	11 Prod
Operating Conditions:										
Temperature, °F	326		311		311		327		327	
Contact Time, Min	11.2		10.5		13.2		9.9		12.3	
Vol. Per Cent HF in Reactor	69		55		40		52.5		64	
Diluent	Toluene-Ethylbenzene		Toluene		Toluene		None		None	
Vol. Per Cent Diluent in Feed	47-6		50		50					
Mol. Fraction HF			0.867		0.780		0.864		0.910	
"Raffinate" Phase, Grams	820		3,082		4,160		917			
HF Extract:										
Grams	16		33		36		18		20	
Bromine No.	4		4		5		10		6	
Compositions, Vol. Per Cent:										
Benzene		1.9_6								
Toluene	47	45.9	50.0	50.3	50.0	49.6	0.4_2	2.0_5	0.4_3	2.4_3
Ethylbenzene	6	2.5								
Orthoxylene		5.6		3.7		1.5		3.7		9.6
Meta Xylene	45.6	30.8	48.6	39.1	48.6	45.1	97.1	82.9	97.1	70.2
Para Xylene		8.8		6.3		3.3		9.2		15.3
Bottoms	0.1_8	3 to 1.5 $C_9{+}C_{10}$	0.1_9	0.5_6	0.1_9	0.5_8	0.3_8	2.1_6	0.3_8	2.4_8
Xylene Fraction, Vol. Per Cent:										
Ortho		12.3		7.5		3.0		3.9		10.1
Meta		68.1		79.6		90.4		86.5		73.8
Para		19.6		12.9		6.6		9.6		16.1
Per Cent of Max. Para Xylene Produced	93									
Specific Rate Constant, $m{\to}p$, k_1	.040		.0184		.0056		.0131		.0238	
Specific Rate Constant, Disproportionation, k_2			.00143		.00099		.00167		.00191	

NOTE.—Figures appearing as subscripts in the above table are observed analytical values of doubtful accuracy.

TABLE III

Isomerization of xylenes by HF-tubular reactor

Example No.	12		13		14		15		16	
Operating Conditions:										
Temperature, °F.	328		328		328		347		349	
Contact Time, Min.	12.4		12.2		9.9		12.4		13.8	
Vol. Per Cent HF in Reactor.	66		64.6		80.3		65		69	
Water Added, Wt. Per Cent of HF Catalyst [1]	4.2₄		2.0₄		2.0₄		2.0₄		None	
Diluent.	None		None		None		None		C₉+Bottoms Toluene 5.0–47.5	
Vol. Per Cent Diluent in Feed.	0.87		0.89		0.931		0.888		0.935	
Mol. Fraction HF.	1,102									
"Raffinate" Phase, Grams.										
HF Extract:										
Grams.	12.5		14.5		6.5		17.0		25.0	
Bromine No.	5									
	Feed	**Prod.**	**Feed**	**Prod.**	**Feed**	**Prod.**	**Feed**	**Prod.**	**Feed**	**Prod.**
Compositions, Vol. Per Cent:										
Benzene.										
Toluene.	0.4₂	1.4₉	0.4₂	2.7₂	0.4₂	2.6₉	0.3₁	1.7₃	47.5	47.6
Ethylbenzene.		4.5		6.1		7.7		9.1		6.7
Ortho Xylene.	97.1	83.1	97.1	78.1	97.1	71.5	98.4	73.9	47.5	30.4
Meta Xylene.		9.3		10.1		14.9		13.2		9.8
Para Xylene.	0.3₂	1.7₄	0.3₂	2.9₃	0.3₂	3.1₉	0.3₀	2.0₂	5.0	5.6₄
Bottoms.										
Xylene Fraction, Vol. Per Cent:									14.3	
Ortho.		4.6		6.5		8.2		9.5		64.8
Meta.		85.8		82.8		76.0		76.8		20.9
Para.		9.6		10.7		15.8		13.7		
Specific Rate Constant, m→p, k_1.	.0095		.0122		.0250		.0190		.0461	
Specific Rate Constant, Disproportionation, k_3.	.00096		.00232		.00264		.00203			

[1] The "Anhydrous" HF used in these experiments contained 0.3–0.4% H₂O.
NOTE.—Figures appearing as subscripts in the above table are observed analytical values of doubtful accuracy.

In Table I, Examples 3, 4 and 5 illustrate the benefits of successive increases in the relative proportion of hydrogen fluoride catalyst, and Example 7 in Table II reveals that formation of bottoms boiling above the xylene is reduced approximately two-thirds by toluene as a diluent. Examples 8 and 9 establish that reduction of catalyst content from 55 to 40% greatly reduces the specific reaction rate. Analogous benefits from increase in proportion of hydrogen fluoride catalyst are obtained at higher temperatures as illustrated by Examples 10 and 11. The effect of small amounts of water in the hydrogen fluoride catalyst are revealed in Table III, Examples 12–15 inclusive. Note that in Example 15, decrease in catalyst activity due to the presence of water is largely mitigated by a mild increase in temperature. Suppression of the formation of disproportionation products boiling above the xylenes is illustrated in Example 16, wherein the isomerization was effected in the presence of 5% of C₉ and higher boiling bottoms fraction as well as in the presence of toluene. The data show that disproportionation in this example was low, since the bottoms fraction increased only by .64% despite the fact that the temperature was sufficiently high to increase relative disproportionation rates.

Fig. 4 is a graph of specific rate constants (k_1) of isomerization versus mol fraction of hydrogen fluoride for reactions carried out at three different temperatures. Fig. 5 is a corresponding plot of specific rate constants (k_3) for disproportionation versus mol fraction of hydrogen fluoride at the same three temperatures. These graphs are for xylene isomerization and disproportionation respectively. It will be noted that the specific rate constant for isomerization is in the order of ten fold greater than the specific rate constant for disproportionation in the process of this invention and that the isomerization reaction rate increases greatly with mol fraction of hydrogen fluoride catalyst.

The applicability of hydrogen fluoride as a catalyst for isomerization of dialkyl benzenes other than dimethyl benzene is illustrated by the data in Table IV:

TABLE IV

Isomerization of para-cymene with HF

Example No.	17		18	
Charge, Gm.:				
HF.	202		200	
Cymenes.	341		512 (33.3 vol. %, toluene)	
Toluene.				
Operating Conditions:				
Temp., °F.	193–203		197–202	
Contact time, Min.	10		60	
Pressure, p. s. i. g.	146		148	
	Feed	**Product**	**Feed**	**Product**
Water washed product, Vol. per cent:				
Toluene.		3.5	33.3	35
Ortho Cymene.		1.3		1
Meta Cymene.		9.5		37
Para Cymene.	100	85.7	66.7	27
Material balance, Wt. per cent:				
Per cent Hydrocarbon in Raffinate Phase.		96.7		95.9
Per cent Hydrocarbon in Acid Phase.		1.5		1.1

Attention is directed to the fact that this isomerization is effected under milder conditions with the propyl group of cymene than is required for the methyl groups of the xylenes.

Although hydrogen fluoride alone is preferred as a catalyst, at present, it is to be understood that activators or modifiers of the hydrogen fluoride are not outside the broader aspects of the invention. For example, temperatures required for isomerization may be reduced below 250° F. by addition of an activator, such as BF₃ in small amounts, to the hydrogen fluoride catalyst.

It is readily apparent from the foregoing description that various modifications of the process and apparatus can be made within the spirit of

the present invention and the scope of the amended claims. In the drawings various details, such as pumps, valves, pressuring means, coolers and heat exchangers have in some instances been omitted. Any suitable form of apparatus incorporating these necessary details as well as utilizing appropriate corrosion-resistant metals and alloys can be supplied in obvious manner by those skilled in the art.

I claim:

1. A continuous process for isomerizing a xylene comprising the steps of blending a xylene charging stock and at least 10% by volume of toluene with anhydrous liquid hydrogen fluoride, at a temperature of 250° to 400° F., the proportion of said hydrogen fluoride being equal to 40% to 90% of the total liquid mixture thus forming a single liquid phase blend, thereafter immediately passing said blend through a reaction zone in non-turbulent flow, whereby the mixture downstream is substantially unmixed with the upstream reaction mixture, maintaining the temperature at about 250° to 400° F. in said reaction zone, cooling the reaction product mixture effluent from the reaction zone to separate a hydrocarbon phase and an acid phase, separating the hydrocarbon phase from the acid phase, fractionally distilling the hydrocarbon phase to separate a toluene fraction, a xylene fraction, and a higher boiling fraction comprising side reaction products and re-

turning at least a portion of the toluene fraction and of the higher boiling fraction to the blending step together with further quantities of liquid xylenes and hydrofluoric acid.

2. The process as defined in claim 1 wherein the temperature in the reaction zone is maintained in the range about 310 to 350° F.

3. The process as defined in claim 1 wherein the proportion of hydrogen fluoride employed is equal to 60 to 85 per cent by volume of the total liquid mixture.

4. The process as defined in claim 1 wherein the temperature in the reaction zone is maintained in the range about 310 to 350° F. and the proportion of hydrogen fluoride employed is equal to 60 to 85 per cent by volume of the total liquid mixture.

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