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CATALYSIS OF ALKYL AROMATIC ISOMERIZATION

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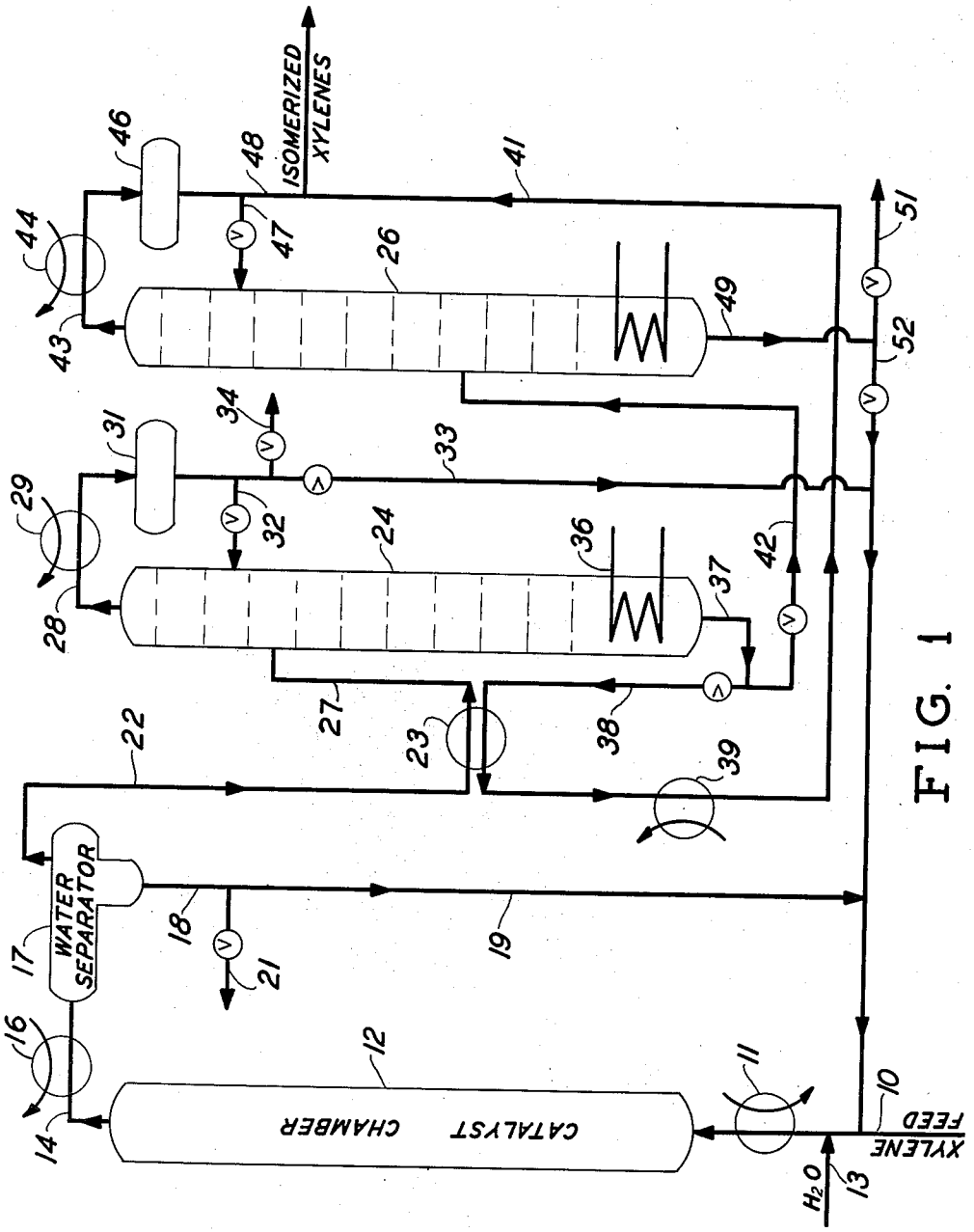


FIG. 1

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CATALYSIS OF ALKYL AROMATIC ISOMERIZATION

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The present invention relates to catalytic isomerization of aromatic compounds containing a plurality of saturated side chains and more particularly to catalyzing the shifting of intact aliphatic 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 isomerization at the ring or nucleus to distinguish from mere isomerization of aliphatic to aliphatic carbon bonds in an aliphatic chain or of aromatic to aromatic carbon bonds in the cycle structure of the ring itself.

The invention is particularly applicable to and finds its greatest present utility in the isomerization of dialkyl benzenes, more notably dialkyl benzenes in which at least one alkyl group is methyl, and especially xylenes. 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-substituted 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 reference to the more difficult isomerization, i. e., catalyzing the shift of methyl groups at the benzene ring as in the xylenes.

Flexibility and economical utilization of alkyl aromatic hydrocarbons introduces a need for an efficient process for conversion of alkyl aromatic compounds from one isomeric form to another. Thus, ortho xylene 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 ortho xylene as blending agents or additives for certain special motor fuels, and the supply of this superior blending agent could be enhanced by isomerization of ortho xylene. 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 production of the para isomer there

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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 desirable to provide a process for isomerization of ortho or para xylenes or both to the meta isomer.

This invention involves catalysis of the foregoing desired isomerization reactions with phosphoric acid. The catalytic action of phosphoric acid in isomerization of this type can be made highly selective for the desired shifting of substituents at the ring. Thus, the isomerization of xylenes by phosphoric acid catalysis may be effected with a minimum of side reactions, such as disproportionation and formation of trimethyl benzenes and toluene. The catalytic action of phosphoric acid 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 pressures.

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 isomerization 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 necessitates adequate suppression of side reactions.

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 over-all conversions and yields can be obtained by removing a substantial pro-

portion of a 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.

Suitable conditions for catalyzing isomerization of alkyl aromatic hydrocarbons by means of a phosphoric acid catalyst in accordance with the present invention will be apparent from the following. A temperature of from about 600° F. to about 1100° F. normally will be found operative for isomerization of xylenes. Somewhat lower temperatures are appropriate where higher alkyl groups are involved. Thus, 400–1000° F. is appropriate for diethyl and higher alkyl benzenes. For the isomerization of xylenes, a temperature of from about 700–900° F. is desirable, and depending upon catalyst activity a temperature of from about 725–850° F. is presently regarded as optimum. It is to be understood that less severe conditions, that is, lower temperatures or lower contact times, or both, are acceptable for isomerization of ethyl and higher molecular weight aliphatic side chains. Such higher alkyl groups are more easily isomerized at the aromatic nucleus than are methyl groups. Likewise, lower temperatures and lower contact time within the ranges given are more effective with catalysts of higher activity, and loss in catalyst activity may be compensated in part by elevation of reaction temperatures or increase in contact times or both.

The phosphoric acid catalyst preferably is orthophosphoric acid, and desirably is of the type known as a solid phosphoric acid. Such solid phosphoric acid catalysts comprise orthophosphoric acid on a suitable porous carrier such as kieselguhr, activated carbon or the like. The inclusion of small amounts of metal salts as modifiers, for example, zinc, cadmium, or copper phosphates is not precluded. The broader aspects of the invention embrace liquid phosphoric acid catalysts of various types, and particularly liquid phosphoric acid films on non-porous carriers, such as quartz.

Maintenance of acid catalyst strength at approximately 100% orthophosphoric acid by addition of steam or water to hydrocarbon feed is preferred. However, phosphoric acid catalyst of lower strength, for example, 95% acid or of higher acid strength resulting from partial dehydration, for example, 110% orthophosphoric acid are not precluded.

Contact time for a given conversion in the isomerization reaction is a function of temperature, catalyst activity, and feed composition. Ordinarily a minimum of about five seconds will be required and a maximum contact time of sixty minutes need not be exceeded. Generally one to fifteen minutes will suffice. It is to be understood that pressure and space rates fix contact times at a given temperature and the foregoing contact times are calculated on the basis of a solid phosphoric catalyst containing 60% free space.

Pressure is not critical; reaction normally will be in vapor phase but liquid phase reactions will occur at higher pressures and lower temperatures within operative ranges. Pressures of from atmospheric to 3,000 pounds per square inch are suitable, but from 100–1,000 pounds per square inch is more desirable and 250–500 pounds per square inch is presently preferred.

Space rates may vary from 0.05 to 5.0 liquid volumes of hydrocarbon feed per volume of catalyst per hour. More desirably, space rate is from 0.1 to 2.0 and preferably from 0.25 to 1.0 liquid volumes of hydrocarbon feed per volume of catalyst per hour.

Diluents are not necessary but may be utilized to suppress side reactions, such as disproportionation. Hydrogen is an excellent diluent, since it also tends to suppress coke formation and increase catalyst activity. Toluene may be utilized as a diluent to reduce any tendency to form disproportion products by side reactions particularly under more severe operating conditions.

In accordance with the invention ortho xylene may be produced by feeding a xylene fraction containing less than equilibrium proportions of ortho xylene through a phosphoric acid isomerization zone under isomerization conditions such as above disclosed. The shift of methyl groups along the benzene ring is catalyzed by the orthophosphoric acid to form ortho xylene and yield a mixture of xylene isomers enriched in ortho xylene content as compared with the feed. The reaction mixture is suitably fractionated to yield a purified xylene fraction which is passed to an ortho xylene recovery unit. Ortho xylene or an ortho xylene rich fraction may be separated by distillation. Close distillation as by superfractionation will yield an ortho xylene product of 95% or higher purity as a bottoms fraction. However, for some purposes a 70–90%, or more desirably an 85–95% ortho xylene rich product is acceptable.

The ortho xylene poor overhead fraction from the superfractionating or other distillation unit may be recycled to the isomerization zone and thereby effect conversion of additional meta and para xylenes to the ortho xylene isomer.

A para xylene product may be prepared by feeding to the phosphoric acid isomerization system a suitable xylene fraction, such as ortho xylene, meta xylene, a mixture of ortho and meta xylene or a mixture of xylenes containing a smaller proportion of para xylene than is present in the isomerized reaction product. Isomerization effluent may be purified and treated for recovery of the para isomer. A suitable method for recovery of para xylene is selective crystallization. The para xylene product may be crystallized from the mixed xylene fraction by chilling to a temperature of at least about −50° F. and preferably to about −65° F. 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. The presence of paraffinic and/or other aromatic hydrocarbon constituents lowers the permissible crystallization temperature. 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. The para xylene poor mother liquor from the crystallization may be recycled to the phosphoric isomerization zone to increase the production of the para isomer.

In similar manner the production of meta xylene involves isomerization of a suitable xylene fraction followed by separation of a meta xylene product from the resulting isomerized mixture. A suitable method for separating or recovering meta xylene from the mixture of xylenes in the

isomerization effluent involves selective sulfonation to selectively form a meta xylene sulfonic acid phase and a supernatant oil layer containing predominantly ortho and para xylenes. These phases are separated 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 xylene sulfonic acids may be hydrolyzed to recover ortho and para xylenes. These recovered xylenes together with the unsulfonated ortho and para xylene fraction are recycled to the isomerization zone and converted to the selected isomer.

In the drawing, one suitable form of isomerization unit for practicing the process of this invention is illustrated.

As shown in the figure of the drawing, xylene feed enters the isomerization system through inlet line 10, is raised to reaction temperature by preheater 11 and flows therefrom to a fixed bed, phosphoric acid isomerization catalyst chamber 12. To prevent excessive dehydration of the phosphoric acid catalyst water or steam is introduced into the xylene feed via line 13. The amount of water so injected is controlled to maintain the phosphoric acid catalyst at desired concentrations previously disclosed.

An example of suitable operating conditions in an isomerization chamber using a solid phosphoric acid catalyst comprising orthophosphoric acid of approximately 100% strength supported on kieselguhr is about 700° F. catalyst temperature and about 500 p. s. i. g. pressure. A space rate of 0.1 liquid volumes of hydrocarbon feed per volume of catalyst per hour yields a mixture of xylenes containing about 19% para xylene.

The isomerized xylene mixture then flows from catalyst chamber 12 through outlet conduit 14 by way of condenser 16 to a water separator 17 where the condensate is allowed to stratify into an upper xylene layer and a lower water layer. The water layer is withdrawn through conduit 18 and may be returned to xylene feed through line 19 or discarded, as indicated, by valve controlled line 21. Xylenes from the water separator 17 pass through conduit 22 and heat exchanger 23 to purification section.

In the process here illustrated, the reaction mixture is purified first by fractionation in column 24 to eliminate lower boiling hydrocarbons such as toluene and/or any volatile diluent. All or part of the topped xylene mixture is preferably then fractionated in column 26 to yield a xylene heart cut as overhead and higher boiling impurities or reaction products as bottoms. Thus the reaction mixture enters fractionating column 24 by way of inlet line 27 and a toluene overhead cut flows from the top of the fractionating column through line 28, condenser 29 to reflux drum 31, from which controlled portions may be returned to fractionator 24 through valve controlled reflux line 32. The remaining toluene distillate flows from reflux drum 31 and may be recycled to isomerization feed by way of valve controlled line 33 in order to furnish a diluent which serves to suppress possible side reactions, such as disproportionation. A portion of the toluene overhead may be withdrawn through line 34 as a means of controlling the relative proportions of toluene diluent and xylene feed.

Heat is supplied to fractionator 24 by any suitable means, here shown as steam coil 36. The topped xylenes flow from the bottom of fractionator 24 through outlet line 37 and may pass in either or both of two directions. In single pass operation when the amount of higher boiling side reaction products is small, all of the xylenes may flow through valve control line 38, heat exchanger 23, cooler 39 and line 41 to product storage. When the amount of higher boiling impurities or side reaction products are relatively large or when a cyclic operation is involved, a xylene heart cut will be taken by conducting the xylene bottoms from fractionator 24 through valve controlled line 42 to fractionator 26. Impurities tend to accumulate or build up in a cyclic system such as previously described, i. e., one in which the xylenes from the isomerization are passed through an isomer separation stage and residual xylenes recycled to isomerization. In such a mode of operation it will be found desirable to control build-up of heavier or higher boiling impurities, even though original impurity content is small for single pass operation, by passing at least a portion of the topped xylene fraction from fractionator 24 to and through fractionator 26.

Topped xylenes entering fractionator 26 from inlet line 42 are distilled overhead and flow through outlet conduit 43, condenser 44 to reflux drum 46. A portion of the overhead may be returned to the top of column 26 by valve controlled reflux unit 47 and the remainder passes by way of line 48 to product storage or isomer recovery treatment, as desired.

Bottoms from fractionator 26 are discharged by way of line 49 and may be removed from the system through valve controlled outlet 51. In various instances it may be found desirable to recycle controlled amounts of these heavier impurities to the isomerization feed by way of valve controlled line 52. This mode of operation is particularly useful when and if the isomerization reaction is conducted under relatively severe conditions which tend to increase the amount of disproportionation products formed. This tendency to form disproportionation products may be suppressed or reduced by recycle of such disproportionation products from the bottom of fractionating column 26.

Reference has been made to the provision of diluents in the isomerization reaction zone. The presence of diluents miscible with the hydrocarbon reaction mixture increases the selectivity for, or selectively promotes the isomerization reaction, i. e., the same fractional conversion 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 such diluents. Toluene as a diluent reduces losses by disproportionation of xylenes over and above the reduction obtained with substantially inert diluents, such as propane or cyclopentane. For these reasons it is preferred to effect the isomerization reaction in the presence of a diluent, more desirably toluene, with xylene isomerization when and if the isomerization conditions are sufficiently severe to otherwise cause disproportionation of objectionable magnitude. With dialkyl benzenes other than xylenes, the preferred diluent is a monoalkyl 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 hydrocarbon feed. Preferably toluene will be present in proportions not substantially less than those formed by dis-

proportionation to equilibrium, e. g., 30 to 60% by volume of xylenes.

Further to guide those skilled in the art in the practice of this invention and to exemplify the catalytic action of phosphoric acid in the isomerization of dialkyl benzenes, illustrative data are given in Table I.

TABLE I

Xylene isomerization

Example No.	(1)	(2)	(3)	(4)	(5)	(6)
Operating Conditions:						
Temperature, °F.	650	700	750	750	750	700
Pressure, p. s. i. g.	500	500	500	500	500	500
Feed Rate, Liquid V/V/Hr.	0.25	0.25	0.25	1.0	0.25	0.1
Diluent/Xylene, Mole Ratio	-----	1.9	1.9	1.9	1.9	1.2
Feed, Mole Per Cent:						
Ethyl Benzene	1.7	-----	-----	-----	-----	-----
o-xylene	90.8	-----	-----	-----	-----	-----
m-xylene	6.1	98	98	98	98	98
p-xylene	1.4	-----	-----	-----	-----	-----
Composition of Xylene Fraction:						
Ethyl Benzene	4.6	0	0	0	0.2	0.2
o-xylene	76.4	8.3	10.3	7.2	8.8	15.4
m-xylene	16.0	82.6	76.9	84.2	78.6	66.5
p-xylene	3.0	9.1	12.8	8.6	12.4	17.4

In all of the examples of Table I the catalyst was of the solid phosphoric acid type, more particularly ortho phosphoric acid on a kieselguhr support.

The applicability of phosphoric acid catalyst to isomerization of other alkyl aromatic compounds is illustrated by the isomerization of p-cymene with phosphoric acid on kieselguhr under the following conditions:

Temperature, 510° F.
Pressure, p. s. i. g., 500
Feed rate, liquid V./V./Hr., 1.4
Diluent, toluene
Diluent/xylene, mole ratio, 2:1
Composition of isomerized cymene fraction:
o-cymene, 3.3% by volume
m-cymene, 12.0% by volume
p-cymene, 84.7% by volume.

Ethyl benzene is relatively unaffected by the phosphoric acid catalyst under the isomerization conditions in the foregoing illustrative examples. Accordingly, it will be desirable to provide for control of ethyl benezene build-up when and if a cyclic type operation is utilized for production of a single xylene isomer with recycle of residual xylenes to isomerization feed. Xylenes of commercial purity normally contain ethyl benzene as an impurity and ethyl benzene build-up becomes excessive in such cyclic processes. Any suitable method for controlling or reducing ethyl benzene build-up may be used. One such method is crystallization of the xylenes and separation from ethyl benzene which has a lower freezing point. Another method is by disproportionation of the ethyl benzene and distillation to remove the resulting lower and higher disproportionation products. Various commercial xylenes also may contain unsulfonatable hydrocarbon impurities commonly designated paraffinic. Such impurities can be eliminated if desired by any suitable treatment of the feed prior to isomerization. In a cyclic type operation either the feed or recycle stock from the xylene isomer recovery stage, or both the fresh xylene feed and a portion of the recycle stock may be treated for elimination or reduction of unsulfonatable hydrocarbon impurities. One suitable method comprises an extractive distillation process such as disclosed in Cope et al. Patent No. 2,215,915, issued September 24, 1940.

It is readily apparent from the foregoing description that various modifications of the process can be made within the spirit of the present invention and the scope of the appended claims. For the sake of simplicity and clarity, the drawings have illustrated only major unit operations in the process and details such as pumps, valves, pressuring means, coolers, heat exchangers and the like have been omitted. Any suitable form of apparatus incorporating these necessary details can be supplied in obvious manner by those skilled in the art.

I claim:

1. A process for isomerizing a dialkyl benzene having not more than 3 carbon atoms in each alkyl group which comprises contacting said dialkyl benzene with a solid isomerization catalyst containing phosphoric acid at a concentration in the range 95 to 110% calculated as ortho-phosphoric acid as the effective catalytic material at a temperature in the range 400° F. to 1100° F. and at a space velocity in the range 0.05 to 5.0 volumes of liquid dialkyl benzene per volume of catalyst per hour the temperature within said temperature range being at least 600° F. when the dialkyl benzene is xylene.

2. The method as defined in claim 1, wherein the dialkyl benzene is a methylalkyl benzene having 1 to 3 carbon atoms in the alkyl group.

3. The method as defined in claim 1, wherein the dialkyl benzene is a xylene.

4. The method as defined in claim 1, wherein the dialkyl benzene is contacted with the catalyst in the presence of toluene in amount sufficient to constitute 10 to 50% of the total hydrocarbon charge.

5. A continuous process for isomerizing a xylene feed with a solid isomerization catalyst containing phosphoric acid at a concentration in the range 95 to 110% calculated as ortho-phosphoric acid as the effective catalytic material in an isomerization zone at a temperature in the range 700 to 900° F., at a space velocity in the range 0.1 to 2.0 volumes of liquid xylene feed per volume of catalyst per hour, and introducing into the isomerization zone together with the feed a small amount of water sufficient to maintain the concentration of the acid catalyst within said concentration range.

6. The method as defined in claim 5, wherein the phosphoric acid catalyst is disposed on a porous solid support.

7. The method as defined in claim 5, wherein the phosphoric acid is supported on kieselguhr.

8. The method as defined in claim 5, wherein the phosphoric acid is disposed on a non-porous support.

9. The method as defined in claim 5, wherein the phosphoric acid is disposed on quartz.

10. The method as defined in claim 5, wherein toluene is introduced into the isomerization zone together with the feed in amount sufficient to constitute 10 to 50% of the total hydrocarbon material introduced into the isomerization zone.

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