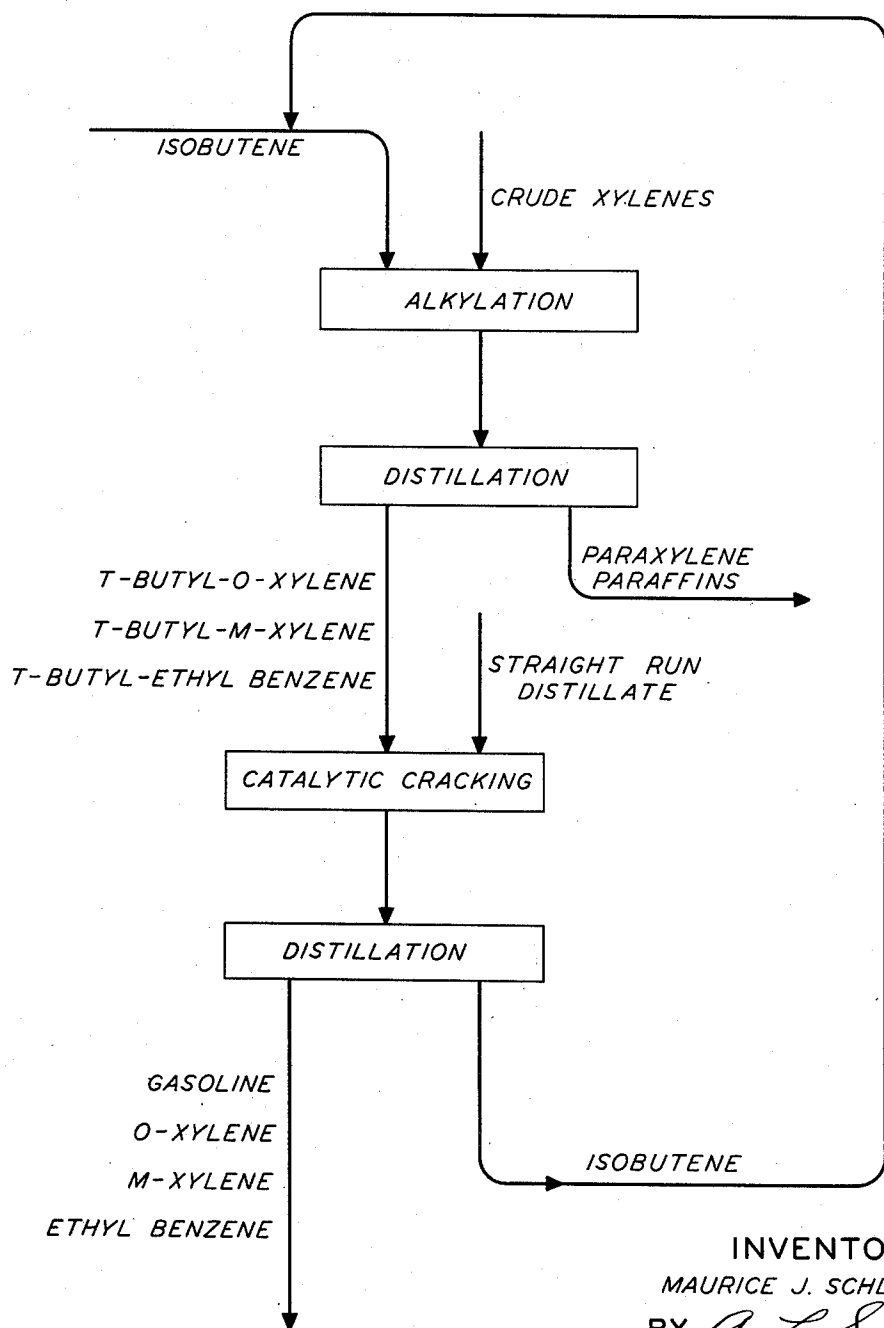


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XYLENE SEPARATION PROCESS

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XYLENE SEPARATION PROCESS

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This invention relates to an integrated process for recovering individual xylene isomers from crude xylenes and producing a blended high octane gasoline containing the undesired xylene isomers.

Crude xylene fractions are produced in commercial quantities by hydroforming naphthenic petroleum distillates and by fractionating the liquid product produced during the coking of coal. The crude xylenes produced by either of these methods contain the three xylene isomers in approximately equilibrium concentrations and substantial amounts of ethylbenzene which cannot readily be separated from the xylenes by fractional distillation. The crude xylene produced during the coking of coal consists almost entirely of aromatic hydrocarbons, while the crude xylene produced by hydroforming naphthenic petroleum distillates usually contains about 10% of paraffinic hydrocarbons boiling in the boiling range of the xylenes. The least valuable of the xylene isomers for the purpose of upgrading gasoline is ortho-xylene.

This isomer may be separated from the crude xylene by fractional distillation and oxidized to phthalic anhydride.

Recently, the separation of para-xylene from the crude xylene fraction has been practiced to supply commercial demands for terephthalic acid produced by oxidation of para-xylene. Para-xylene has been separated from the crude xylene fractions by fractional crystallization. After separation of the ortho-xylene or the para-xylene, or both, from the crude xylene fraction, the remainder of the fraction has been used as a gasoline blending stock in the production of high octane gasolines.

It has now been found that the separation of para-xylene and ortho-xylene from a crude xylene stock, and the blending of the residue of the stock with gasoline to improve its octane rating, may be effected readily and economically by the new process described herein.

Pursuant to the invention, either a crude xylene stock or a crude xylene stock which has been fractionally distilled to reduce its ortho-xylene content is contacted with isobutene in the presence of an alkylation catalyst under alkylating conditions. The ortho-xylene, meta-xylene and ethylbenzene contained in the crude xylene are readily alkylated with isobutene to produce the higher boiling tertiary-butyl derivatives of these materials. Para-xylene resists the introduction of the tertiary-butyl group and comes through the alkylation process unchanged. The alkylation reaction product is fractionally distilled to

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separate an overhead fraction consisting predominantly of para-xylene and a bottoms fraction comprising tertiary-butyl-meta-xylene, tertiary-butyl-ethylbenzene, and tertiary-butyl-ortho-xylene. The bottoms fraction is then contacted with a catalytic cracking catalyst at a temperature above about 600° F. and it is found that the tertiary-butyl group is quite selectively cracked from the tertiary-butyl xylenes and tertiary-butyl-ethylbenzene to produce predominantly isobutene and the xylenes. The isobutene is separated from the reaction product of the cracking step and returned to the alkylation step together with further quantities of the crude xylene feed.

The contact of the bottoms fraction of the alkylation reaction product with the cracking catalyst is desirably accomplished simply by feeding this bottoms fraction together with a usual cracking charge stock to a catalytic cracking zone. For example, this fraction may be fed to a catalytic cracking zone together with a straight run gas oil boiling in the range about 400 to 850° F. In the cracking zone both the alkylation bottoms fraction and the gas oil are contacted with a cracking catalyst, for example, a silica-alumina bead catalyst, at temperatures in the range 800 to 1000° F. In the cracking zone the gas oil is cracked in the usual manner and the tertiary-butyl groups are cracked from the components of the alkylation bottoms fraction. The total reaction product is then fractionally distilled to separate an isobutene fraction which is returned to the alkylation step and a gasoline fraction comprising the usual components of a gasoline derived from a catalytically cracked gas oil and, in addition, xylenes and ethylbenzene.

The alkylation bottoms fraction may also be charged to a catalytic cracking or treating zone in which thermally cracked naphtha, for example, a naphtha boiling in the range about 280 to 600° F., is being treated by contacting it with a silica-alumina cracking catalyst at temperatures in the range about 800 to 950° F. to upgrade the thermally cracked naphtha by desulfurizing it, increasing its gum stability, and cracking the higher boiling fractions of the naphtha. In this catalytic treating step, the alkylation bottoms fraction is cracked to liberate isobutene, xylenes, and ethylbenzene. The treated naphtha and alkylation bottoms are fractionally distilled to separate an isobutene fraction which is then returned to the alkylation step together with further quantities of crude xylene and a gasoline fraction comprising the usual gasoline components of the treated naphtha, xylenes and ethylbenzene.

The alkylation step of the process of the invention is illustrated by the following example.

EXAMPLE 1

A xylene fraction separated from catalytically reformed naphtha was contacted with isobutene in the presence of substantially anhydrous hydrogen fluoride at a temperature of 0 to 10° C. for a period of 4 hours. The xylene mixture introduced into the alkylation zone contained 14% ethylbenzene, 8% ortho-xylene, 48% meta-xylene, 18% para-xylene, and 12% of paraffins boiling in the boiling range of the xylenes. The amount of isobutene introduced into the alkylation zone was somewhat

less than the amount stoichiometrically required to alkylate all of the aromatic hydrocarbons present in the xylene fraction. After the alkylation reaction was complete, a C₈-fraction was distilled from the reaction product. Analysis of this fraction showed it to contain 6% of the ethylbenzene, 12% of the ortho-xylene, 16% of the meta-xylene, 94% of the para-xylene, and 76% of the paraffins, which had been present in the xylene fraction fed to the alkylation zone. It is evident that relatively little of the ethylbenzene, ortho-xylene and meta-xylene remained unalkylated, while very little of the para-xylene was consumed in the reaction. This C₈-fraction, separated from the alkylation reaction product, consists predominantly of para-xylene and pure para-xylene may be readily recovered from it by fractional crystallization. The alkylation reaction product may be separated into two fractions, a C₈-fraction rich in para-xylene and a bottoms fraction which is then contacted with a catalytic cracking catalyst under catalytic cracking conditions. If desired, the bottoms fraction may be recovered in separate cuts, for example, one cut containing 1,3-dimethyl-5-tertiary-butylbenzene and small amounts of meta-tertiary-butylethylbenzene, which boil at 205 and 206° C. and may be recovered in a narrow boiling fraction; a second cut containing 1,2-dimethyl-5-tertiary-butylbenzene and para-tertiary-butylethylbenzene boiling at 215° C. and 211° C.; and a cut comprising 3,5-di-tertiary-butylethylbenzene boiling at 260° C. and di-tertiary-butylbenzene. One or more of these cuts may be processed for the recovery of particular aromatics and the remainder of them contacted with the cracking catalyst under cracking conditions.

The manner in which the bottoms fraction from the alkylation reaction product may be broken up into the original aromatic hydrocarbons and isobutene is illustrated in the following Example 2. In order to obtain a material balance and illustrate the relationship between the reaction product and the reactants, this example shows the effect of contacting one of the components of the alkylation bottoms fraction, i. e., 1,3-dimethyl-5-tertiary-butylbenzene, with a silica-alumina catalyst.

EXAMPLE 2

The catalytic cracking apparatus consisted of a 1 inch x 12 inch Pyrex preheater chamber filled with quartz fragments and sealed through a narrower tube to a 1 inch x 18 inch catalyst chamber. The preheater and catalyst chamber were equipped with thermocouple wells and surrounded by electrically heated furnace sections.

The feed stock was metered into the upper preheater section of the vertical assembly and the effluent stream passed through a spiral condenser maintained at 60° F. into an ice-cooled receiver. The effluent stream from the receiver passed into a "dry ice" cooled trap and to a gasometer.

The apparatus was flushed with nitrogen prior to each run. Carbonized material was determined by raising the temperature to 975° F., while passing air through the apparatus. The carbon dioxide formed was absorbed in "Ascarite" (potassium hydroxide on asbestos) and weighed.

The catalyst used was an equilibrium T. C. C. bead catalyst consisting of 10% alumina and 90% silica, the average diameter of the beads was 0.125–0.13 inch.

The product collected in the "dry ice" cooled traps was vaporized and representative samples analyzed in the mass spectrometer. The liquid product collected in the ice trap was distilled in a low temperature Podbielniak column and the C₁ to C₅ fraction analyzed in the mass spectrometer. The bottoms were distilled through a semi-micro concentric tube column to separate the xylene fraction. Freezing point analysis of the xylene fractions gave values of 97.7% and 98.1% meta-xylene, respectively. Reaction conditions and product analyses are shown in Table I.

Table I

Process Data:		653-43I	653-43II	
Run No.				
Space Rate, V./V./hr.		2.0	4.0	
Catalyst-Oil Ratio, V./V.		2.0	2.0	
Reactor Wall Temp., °F.		750	750	
Catalyst Temp., °F.		693	690	
Catalyst Activity (Cat. A)		31.5	31.5	
Weight of Charge, g.		60	60	
Conversion per Pass, Percent.		90	90	
	Wt. Percent of Total Product	Moles per Mole of Charge	Wt. Percent of Total Product	Moles per Mole of Charge
Product Data:				
Fraction Collected at 60° F.	85.95	-----	81.00	-----
Fraction Collected at -100° F.	12.93	-----	17.00	-----
Uncondensed Gas	0.75	-----	0.46	-----
Carbon	1.52	0.206	1.43	0.177
Material Balance	+1.15	-----	-0.11	-----
Product Composition:				
Propene	0.48	0.019	0.41	0.016
Propane	0.08	0.003	0.07	0.003
Isobutane	3.66	0.102	2.80	0.078
n-Butane	0.13	0.004	0.14	0.004
Butenes ¹	24.14	0.698	24.25	0.701
Isobutene	22.38	-----	22.20	-----
1-Butenes	0.91	-----	0.43	-----
2-Butenes	0.95	-----	1.62	-----
Isopentane	0.28	0.006	0.07	0.002
Pentanes	0.80	0.019	0.65	0.015
C ₅ -C ₈	0.48	0.009	0.70	0.013
Total C ₁ -C ₈	30.05	0.860	29.09	0.832
m-xylene ²	58.50	0.894	49.15	0.751
Unchanged Starting Material	10.33	0.103	19.76	0.198
Total Aromatics		0.997	-----	0.949

¹ The total butene value is accurate, but the butene breakdown using only mass-spectrometer data is approximate.

² Freezing point analyses of the total xylene fraction gave values of 97.7% and 98.1% meta-xylene, respectively.

The foregoing example clearly indicates the manner in which tertiary-butyl-meta-xylene is decomposed to yield principally meta-xylene and isobutene by contacting it with a cracking catalyst under cracking conditions. The tertiary-butyl group is similarly removed from tertiary-butylethylbenzene and tertiary-butyl-ortho-xylene at temperatures of 600° F. and above. This cracking reaction may be carried out by introducing the alkylation bottoms fraction into a catalytic cracking unit charging gas oil, straight run naphtha or thermally cracked naphtha. The cracking of the alkylation bottoms fraction proceeds in the presence of these materials in the same manner as illustrated in Example 2. The total cracked product is then fractionally distilled to separate an isobutene fraction which is returned to the alkylation step and a gasoline fraction containing the usual products of the cracking or treating of gas oil or naphtha, as the case may be, plus the aromatic hydrocarbons produced by the cracking of the alkylation bottoms fraction. The octane number of this gasoline is substantially higher than the octane number of the gasoline produced by cracking or treating of gas oil or naphtha by reason of the presence of these aromatics.

The appended drawing illustrates the process flow employed in one modification of the invention. The conditions under which the specific steps can be performed are described below.

The alkylation step of the process can be conducted using not only the hydrogen fluoride catalyst shown in Example 1, but any conventional alkylation catalyst and any conventional set of alkylating conditions.

Catalysts or condensing agents which can be used in the alkylation step include hydrofluoric acid, phosphoric acid, sulfuric acid, Friedel-Crafts catalysts such as zinc chloride, aluminum chloride or ferric chloride, and complexes of Friedel-Crafts catalysts with organic polar liquids such as nitrobenzene, chloroform, and nitromethane. The alkylation reactions are ordinarily conducted at temperatures in the range about minus 10 to plus 100° C. The optimum temperatures for the operable catalysts differ very appreciably, and with some catalysts, such as phosphoric acid on kieselguhr and silica-alumina, may be well above 100° C.

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The catalytic cracking step of the process can be conducted with conventional catalytic cracking catalysts such as the silica-alumina catalysts widely used in the Thermoform catalytic cracking process. Other conventional cracking catalysts such as activated clays and various synthetic catalysts, such as intimate mixtures of two or more metal oxides, such as silica, alumina, magnesia, zirconia, or beryllia, may be employed.

The cracking step should be conducted at a temperature above about 600° F. in order to remove the tertiary-butyl group from the tertiary-butyl aromatic hydrocarbons contained in the alkylation bottoms fraction. When the bottoms fraction alone is charged to the cracking step, temperatures of 600 to 700° F. are adequate. When the alkylation bottoms fraction is charged to the cracking step together with a straight run gas oil, the usual temperatures for the cracking of the gas oil are employed, i. e., from about 850 to 1000° F. When the alkylation bottoms fraction is charged to the cracking step together with thermally cracked naphtha, somewhat lower temperatures commonly employed in this treatment of the naphtha are used, for example, from about 800 to 925° F.

Various modifications of the process above described and illustrated will be apparent to those skilled in the art, which modifications lie within the scope of the invention as defined by the appended claims reciting the essential steps of the process.

I claim:

1. An integrated process for separating xylene isomers and producing high octane gasoline which comprises contacting isobutene with a xylene fraction comprising substantial quantities of para-xylene and meta-xylene in the presence of liquid hydrogen fluoride at a temperature in the range -10 to 100° C., the quantity of isobutene employed being sufficient to alkylate a substantial proportion of the meta-xylene contained in said xylene fraction, fractionally distilling the alkylation reaction product to separate a para-xylene rich fraction and a fraction comprising tertiary-butyl-meta-xylene, contacting the latter fraction and a straight run petroleum distillate with a silica-alumina catalyst in a catalytic cracking zone at a temperature in the range 800 to 1000° F., whereby said latter fraction is cracked forming predominantly meta-xylene and isobutene, fractionally distilling the effluent from the cracking zone to separate a fraction rich in isobutene, and returning the isobutene rich fraction together with additional xylenes to the alkylation step.

2. An integrated process for separating desired components of a crude xylene and concurrently producing a high octane gasoline which comprises contacting isobutene with a crude xylene fraction in the presence of a mineral acid alkylation catalyst at a temperature in the range -10 to 100° C., the quantity of isobutene employed being sufficient to alkylate a substantial proportion of the aromatic hydrocarbons other than para-xylene contained in said xylene fraction, fractionally distilling the alkylation reaction product to separate an unreacted fraction rich in para-xylene and a reacted fraction comprising tertiary-butyl-alkylbenzenes, and contacting the latter fraction and a petroleum distillate with a solid cracking catalyst in a catalytic cracking zone at a temperature in the range 800 to 1000° F. whereby said latter fraction is cracked forming predominantly isobutene and xylenes other than para-xylene.

3. The process as defined in claim 2, wherein the petroleum distillate is a gas oil and the temperature is in the range 850 to 1000° F.

4. The process as defined in claim 2, wherein the petroleum distillate is thermally cracked naphtha and the temperature is in the range 800 to 925° F.

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5. An integrated process for separating desired components of a crude xylene and concurrently producing a high octane gasoline which comprises contacting isobutene with a crude xylene fraction in the presence of a mineral acid alkylation catalyst at a temperature in the range -10 to 100° C. the quantity of isobutene employed being sufficient to alkylate a substantial proportion of the aromatic hydrocarbons other than para-xylene contained in said xylene fraction, fractionally distilling the alkylation reaction product to separate an unreacted fraction rich in para-xylene and a reacted fraction comprising tertiary-butyl-alkylbenzenes, contacting the latter fraction and a petroleum distillate with a solid cracking catalyst in a catalytic cracking zone at a temperature in the range 800 to 1000° F., whereby said latter fraction is cracked forming predominantly isobutene and xylenes other than para-xylene, fractionally distilling the effluent from the cracking zone to separate a fraction rich in isobutene and a gasoline fraction and returning the isobutene fraction together with further quantities of crude xylene to the alkylation step.

6. The process as defined in claim 5, wherein the petroleum distillate is a gas oil and the temperature is in the range about 850 to 1000° F.

7. The process as defined in claim 5, wherein the petroleum distillate is a thermally cracked naphtha and the temperature is in the range about 800 to 925° F.

8. The process as defined in claim 5, wherein the alkylation catalyst is hydrogen fluoride and the cracking catalyst is silica-alumina.

9. A process for the separation of p-xylene from a mixture thereof with ethyl benzene, o-xylene and m-xylene, which comprises subjecting said mixture in the liquid phase to alkylating conditions in the presence of isobutylene and hydrogen fluoride wherein the mole ratio of isobutylene to ethyl benzene, o-xylene, and m-xylene is about 1, whereby said isobutylene alkylates said ethyl benzene, o-xylene, and m-xylene to form the tertiary butyl derivatives thereof, separating p-xylene from the reaction mixture, dealkylating said tertiary butyl derivatives by subjecting said reaction mixture to dealkylating conditions in the presence of a cracking catalyst comprising silica and alumina, to form isobutylene and a mixture of o-xylene, m-xylene and ethyl benzene.

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